RANDOM-WALK THEORY AND STATISTICAL MECHANICS OF LATTICE SYSTEMS

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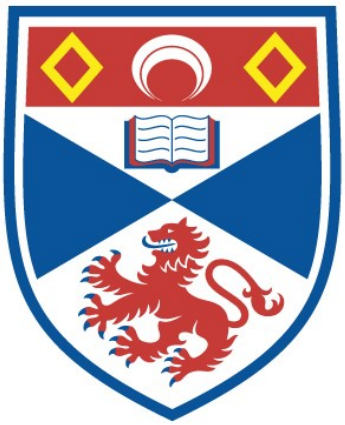

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D E C L A R A T I O N

The accompanying thesis is my own composition. It is based on work carried out by me and no part of it has previously been presented in application for a Higher Degree.

Th 8421

S T A T E M E N T

I certify that the conditions of the Resolution and Regulations have been fulfilled.

Research Supervisor

I was admitted as a Research Student under Ordinance General No. 12 in October 1969, and as a candidate for the degree under this Resolution in October 1970.

A C K N O W L E D G E M E N T S

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C O N T E N T S

A B S T R A C T

It has been found elsewhere that when approximate relations for the two-particle correlation functions of classical statistical mechanics, such as the Percus-Yevick and the mean-spherical approximations, are applied to the lattice gas models with nearest-neighbour interactions simple expressions are obtained for the total correlation function in terms of the lattice Green's function. Since many of the properties of random walks on a lattice can be described by the lattice Green's function, it follows that these systems, at least when treated under these approximations, may be analysed in terms of the language of random walks.

Here the theory of random walks on lattices is appropriately extended to show that the relationship between the correlation functions and the lattice Green's function is not dependent upon the employment of these approximations, nor to a particular range or form of the potential function. Instead, this relationship is shown to be an alternative form of the Ornstein-Zernike relation between the direct and total correlation functions. The direct correlation function is directly related to the probability of a single step, whereas the total correlation function is given by the first-passage-time probabilities of the random walks. Thermodynamic properties, such as the isothermal compressibility, are also interpreted in terms of random-walk concepts.

The random-walk formulation is then extended to include the study of ordered phases in lattice-gas models and hence order-disorder transitions in these systems. Also, an asymptotic form for the lattice Green's function is derived to illustrate how the form of decay of the total correlation function at large distances depends on the properties

of the potential function.

To show that the random-walk interpretation of the Ornstein-Zernike relation is not restricted to lattice systems, we define analogous random-walk functions for continuous space. These lead to a straight-forward generalization of most expressions for discrete space; the relationship between the continuous-space total correlation and Green's functions has the same form as that for the lattice systems. We also explore the possibility of obtaining random-walk properties of a (lattice or continuous-space) system, not from the existing approximate expressions for the direct correlation function, but instead from a generalised Ornstein-Zernike relation based on a maximum principle of classical statistical mechanics.

Finally, we choose a few specific lattice-gas models to show how the method describes their different properties, such as the behaviour of the total correlation function or that of an order-disorder phase transition.

CHAPTER ONE

RANDOM-WALK THEORY AND STATISTICAL MECHANICS OF LATTICE SYSTEMS

1.1 INTRODUCTION

Apparently only recently has the importance of Green's function methods been realised in obtaining closed-form results for the lattice gas and closely related Ising models. The employment of approximations, such as the Percus-Yevick to study the former model[1,2] or the mean-spherical approximation to study the latter model,[3,4] have shown that the correlation function between two particles (or two spins) can be expressed in terms of the lattice Green's function.[5] Parallel to this, and partly motivated by problems in solid-state physics, the theory of random walks on lattices has been developed with the employment of the same Green's function techniques.[6]

It became apparent to us that the introduction of the languages of random-walk processes into the study of the lattice gas (or Ising) model could have several desirable consequences. Firstly, the various aspects of the subject seem to gain more unity from the new framework. Then, too, we have more insight as regards the nature of the different assumptions or approximations proposed. Secondly, by looking at the random-walk properties of specific models, we expect to make progress in the analysis of their most significant features, such as the occurrence of phase transitions. Finally, a similar formulation for continuous systems, apart from its intrinsic value, could provide an explicit link between discrete and continuous-space systems.

It is our intention in this work to show how random-walk concepts enter into the description of the lattice-gas models and their

continuous space analogues. We also attempt to discuss, partially, at least, the consequences derived from the use of these concepts. A preliminary discussion, restricted to extended-core lattice gases with no attractive interactions treated in terms of the Percus-Yevick approximation, has been published.[7]

Throughout these pages, an infinite k-dimensional lattice gas is a collection of particles confined to the sites of an infinite k-dimensional periodic space lattice, whose particles interact through a pairwise potential function. We shall only investigate systems with short range interaction potentials possessing a hard core which excludes multiple occupancy of sites, and which possibly extends to several orders of neighbouring sites. We shall also consider potential functions which, in addition to a hard core, have a soft repulsive or attractive tail.

1.2 RANDOM-WALK THEORY ON PERIODIC SPACE LATTICES. CONCEPTS AND DEFINITIONS.

We shall consider a special class of random walks on infinite k-dimensional periodic space lattices in this and the following chapter. Let us proceed to present the basic language for them.

Let Γ_j represent the set of j-th order neighbour sites to the origin $\underline{s}=\underline{0}$, and let us associate with it a function $P_j(\underline{s})$ which is to represent the probability that any step (from the origin) results in a vector displacement $\underline{s}$ to a j-th order neighbour site and so:

$$P_j(\underline{s}) \neq 0 \quad , \underline{s} \in \Gamma_j$$

$$P_j(\underline{s}) = 0 \quad , \underline{s} \notin \Gamma_j \tag{1.2.1}$$

where

$$\sum_{\underline{s}} P_j(\underline{s}) = 1 \tag{1.2.2}$$

and for a symmetric random walk:

$$P_j(\underline{s}) = \frac{1}{\ell_j} \quad , \underline{s} \in \Gamma_j \tag{1.2.3}$$

where ℓ_j is the number of sites in Γ_j.

A step to a j-th order neighbour is called a <u>j-th order step</u>. In this and the following section we shall consider walks involving steps up to any order. However, we shall later restrict ourselves to walks involving steps up to a definite order m, that is to say, only steps of every order from $j=1$ to $j=m$ are allowed, and from here on we shall also restrict ourselves to walks starting from the origin $\underline{s}=\underline{0}$.

Let $P_n(\underline{s}; \underline{\sigma}_1 \ldots \underline{\sigma}_n)$ be the probability that the walker is

at site $\underline{s}$ after n steps, the i-th step being of order α_i; the $\{P_n(\underline{s};\alpha_1\ldots\alpha_n)\}$ satisfy the recursion formula

$$P_{n+1}(\underline{s};\alpha_1\ldots\alpha_{n+1}) = \sum_{\underline{s}'} P_{\alpha_{n+1}}(\underline{s}-\underline{s}')P_n(\underline{s}';\alpha_1\ldots\alpha_n) \quad . \tag{1.2.4}$$

We now construct a new function, $P_n(\underline{s};\{z_j\})$, from all the n-step functions $P_n(\underline{s};\alpha_1\ldots\alpha_n)$ as follows:

$$P_n(\underline{s};\{z_j\}) = \sum_{\{\alpha_1\ldots\alpha_n\}} P_n(\underline{s};\alpha_1\ldots\alpha_n) z_{\alpha_1}\cdots z_{\alpha_n} \quad , \tag{1.2.5}$$

where the parameter z_j is called the <u>weight</u> of a step of order j. $P_n(\underline{s};\{z_j\})$ is the (unnormalized) probability that the walker is at site $\underline{s}$ after n steps, regardless of the order of the steps involved in the walk. Finally, we define the random walk generating function or lattice Green's function as

$$P(\underline{s};\{z_j\}) = \sum_n P_n(\underline{s};\{z_j\}) . \tag{1.2.6}$$

$P(\underline{s};\{z_j\})$ represents the (unnormalized) probability for the walker to be at site $\underline{s}$ regardless of the number and order of the steps involved in the walk.

We find the Fourier expansions of the functions defined above to be of considerable use. We therefore write:

$$\lambda_j(\underline{\theta}) = \sum_{\underline{s}} P_j(\underline{s})\, e^{i\underline{s}\cdot\underline{\theta}} \quad , \tag{1.2.7}$$

$$W_n(\underline{\theta};\alpha_1\ldots\alpha_n) = \sum_{\underline{s}} P_n(\underline{s};\alpha_1\ldots\alpha_n)\, e^{i\underline{s}\cdot\underline{\theta}} \quad , \tag{1.2.8}$$

$$V_n(\underline{\theta};\{z_j\}) = \sum_{\underline{s}} P_n(\underline{s};\{z_j\})\, e^{i\underline{s}\cdot\underline{\theta}} \quad , \tag{1.2.9}$$

$$U(\underline{\theta};\{z_j\}) = \sum_{\underline{s}} P(\underline{s};\{z_j\})\, e^{i\underline{s}\cdot\underline{\theta}} \quad . \tag{1.2.10}$$

Equations (1.2.2), (1.2.4), (1.2.5) and (1.2.6) now take the following forms:

$$\lambda_j(\underline{\theta}) = 1 \,, \tag{1.2.11}$$

$$W_n(\underline{\theta};\alpha_1 \cdots \alpha_n) = \lambda_{\alpha_1}(\underline{\theta}) \cdots \lambda_{\alpha_n}(\underline{\theta}) \,, \tag{1.2.12}$$

$$V_n(\underline{\theta};\{z_j\}) = \Big[\sum_j z_j \lambda_j(\underline{\theta})\Big]^n \,, \tag{1.2.13}$$

$$U(\underline{\theta};\{z_j\}) = \sum_n \Big(\sum_j z_j \lambda_j(\underline{\theta})\Big)^n = \frac{1}{1 - \sum_j z_j \lambda_j(\underline{\theta})} \,, \Big|\sum_j z_j \lambda_j\Big| < 1 \,. \tag{1.2.14}$$

And hence we have the integral representations:

$$P_n(\underline{s};\{z_j\}) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int \Big[\sum_j z_j \lambda_j(\underline{\theta})\Big]^n e^{-i\underline{s}\cdot\underline{\theta}} d\underline{\theta} \tag{1.2.15}$$

and

$$P(\underline{s};\{z_j\}) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int \frac{e^{-i\underline{s}\cdot\underline{\theta}}}{1 - \sum_j z_j \lambda_j(\underline{\theta})} d\underline{\theta} \tag{1.2.16}$$

for $P_n(\underline{s};\{z_j\})$ and $P(\underline{s};\{z_j\})$. Furthermore, from equation (1.2.14) the reader can observe that the generating function $P(\underline{s};\{z_j\})$ satisfies the Green's function equation

$$P(\underline{s};\{z_j\}) - \sum_{\underline{s}'} \sum_j z_j P_j(\underline{s}-\underline{s}') P(\underline{s}';\{z_j\}) = \delta_{\underline{s},\underline{o}} \,, \tag{1.2.17}$$

where the δ-type term corresponds to the restriction,

$$P_0(\underline{s};\{z_j\}) = \delta_{\underline{s},\underline{o}} \,, \tag{1.2.18}$$

that all walks start from the origin $\underline{s} = \underline{o}$.

We can tidy this up, if we look at the weights z_j as values taken by a function z of the position vector $\underline{s}$ on the lattice, i.e.:

$$z(\underline{s}) = \frac{z_j}{\ell_j} \,, \quad \underline{s} \in \Gamma_j$$

$$z(\underline{o}) = 0 \,. \tag{1.2.19}$$

Then the expression $\sum_j z_j \lambda_j(\underline{\theta})$ is the Fourier expansion $\tilde{z}(\underline{\theta})$ of

the function $z(\underline{s})$, since

$$\sum_j z_j \lambda_j(\underline{\theta}) = \sum_j z_j \sum_{\underline{s}} p_j(\underline{s}) e^{i\underline{s}\cdot\underline{\theta}}$$

$$= \sum_{\underline{s}} \left(\sum_j z_j p_j(\underline{s}) \right) e^{i\underline{s}\cdot\underline{\theta}}$$

$$= \sum_{\underline{s}} z(\underline{s}) e^{i\underline{s}\cdot\underline{\theta}} . \tag{1.2.20}$$

Equations (1.2.15) and (1.2.16) become

$$P_n(\underline{s};z) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int \left(\tilde{z}(\underline{\theta}) \right)^n e^{-i\underline{s}\cdot\underline{\theta}} d\underline{\theta} \tag{1.2.21}$$

and

$$P(\underline{s};z) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int \frac{e^{-i\underline{s}\cdot\underline{\theta}}}{1 - \tilde{z}(\underline{\theta})} d\underline{\theta} , \tag{1.2.22}$$

where we have written z instead of $\{z_j\}$. We call the functions $\lambda_j(\underline{\theta})$ the structure functions of the walk,[6] and the function $\tilde{z}(\underline{\theta})$ the complete structure function of the walk. The function $z(\underline{s})$ itself is referred to as the weight function of the walk.

We shall also need the first-passage-time properties of a random-walker, so that, for this purpose the following concepts are introduced:

Let $F_n(\underline{s};\alpha_1 \cdots \alpha_n)$ be the probability that the walker reaches site $\underline{s}$ after n steps for the first time, the i-th step being of order α_i . $F_n(\underline{s};z)$, the probability that the walker reaches site $\underline{s}$ for the first time, regardless of the order of the steps involved, after the n-th step is defined as

$$F_n(\underline{s};z) = \sum_{\{\alpha_1 \cdots \alpha_n\}} F_n(\underline{s};\alpha_1 \cdots \alpha_n) z_{\alpha_1} \cdots z_{\alpha_n} . \tag{1.2.23}$$

And the first-passage-time generating function is defined accordingly as

$$F(\underline{s};z) = \sum_n F_n(\underline{s};z) \,. \qquad (1.2.24)$$

$F(\underline{s};z)$ is the probability for the walker to be at $\underline{s}$ for the first time independently of the number and order of the steps involved.

The relation between the $F(\underline{s};z)$ and the $P(\underline{s};z)$ generating functions can be obtained when it is observed that if the random walker is at step n he must have been there for the first time at some step i ($i = n$ possibly) and then returned to $\underline{s}$ in $n-i$ steps. We can then write:

$$P_n(\underline{s};\alpha_1 \ldots \alpha_n) = \delta_{n,0}\,\delta_{\underline{s},\underline{o}} + \sum_{i=1}^{n} F_i(\underline{s};\alpha_1 \ldots \alpha_i)\, P_{n-i}(\underline{o};\alpha_{i+1} \ldots \alpha_{n-i}). \qquad (1.2.25)$$

Multiplying the expression above by the corresponding weights, summing over all possible orders of steps and then summing over all possible total numbers of steps n, we obtain

$$F(\underline{s};z) = \frac{P(\underline{s};z) - \delta_{\underline{s},\underline{o}}}{P(\underline{o};z)} \,. \qquad (1.2.26)$$

1.3 THE LATTICE GAS PROBLEM. AN EXACT FORMULATION.

The general problem we set ourselves is a classic one. We aim to derive the thermodynamic properties of an infinite k-dimensional lattice gas assuming knowledge of the potential function governing the interaction of particles in the system.

Of course, the problem has been approached previously and, in principle, solved by the standard methods of classical statistical mechanics. Of these methods the one we use most particularly is that employing the pair correlation functions. Here, we complement this approach by pointing out the simple relations that hold between the pair correlation functions and the random walk functions of the lattice. We hope to exhibit the usefulness of the random walk formalism throughout and, specifically, further ahead when we deal with particular lattice gas models.

For a homogeneous lattice gas, interacting via a pairwise potential, the radial distribution function $g(\underline{s})$ is defined by:

$$g(\underline{s}) = g(\underline{s}_2 - \underline{s}_1) = \frac{\sum_{\{\underline{s}_3, \underline{s}_4 \cdots\}} \exp\left[-\beta \sum_{i<j} \phi(\underline{s}_i - \underline{s}_j)\right]}{\rho^2 \sum_{\{\underline{s}_1, \underline{s}_2, \cdots\}} \exp\left[-\beta \sum_{i<j} \phi(\underline{s}_i - \underline{s}_j)\right]} \qquad (1.3.1)$$

where $\phi(\underline{s}_i - \underline{s}_j)$ is the potential between particles i, and j, ρ is the one-body distribution function, or, more briefly, the density and β is the inverse product of Boltzmann's constant and the temperature.

The total correlation function $h(\underline{s})$ is defined in terms of the radial distribution function $g(\underline{s})$ as

$$h(\underline{s}) = g(\underline{s}) - 1 . \qquad (1.3.2)$$

Also, the direct correlation function $c(\underline{s})$ is defined by the Ornstein-Zernike (OZ) relation[8]

$$h(\underline{s}) = c(\underline{s}) + \rho \sum_{\underline{s}'} c(\underline{s}')\, h(\underline{s}-\underline{s}'). \tag{1.3.3}$$

Thermodynamic properties for the lattice gas can be obtained from the correlation functions through the well known relations:

$$\beta \frac{\partial P}{\partial \rho} = \left[1 + \rho \sum_{\underline{s}} h(\underline{s})\right]^{-1} \tag{1.3.4}$$

and

$$\beta \frac{\partial P}{\partial \rho} = 1 - \rho \sum_{\underline{s}} c(\underline{s}) \,, \tag{1.3.5}$$

where P is the pressure of the system. The problem can be considered solved when knowledge is possessed of the value any of these correlations takes at all interparticle distances $\underline{s}$, for all system densities ρ.

We show now how the lattice Green's function enters into the description of the lattice gas and provides us with a fuller description of the problem.

By introducing the Fourier expansions of the correlations

$$\tilde{h}(\underline{\theta}) = \sum_{\underline{s}} h(\underline{s})\, e^{i \underline{s}\cdot\underline{\theta}} \tag{1.3.6}$$

and

$$\tilde{c}(\underline{\theta}) = \sum_{\underline{s}} c(\underline{s})\, e^{i \underline{s}\cdot\underline{\theta}} \tag{1.3.7}$$

we see that the OZ relation becomes

$$\tilde{h}(\underline{\theta}) = \frac{\tilde{c}(\underline{\theta})}{1 - \rho\, \tilde{c}(\underline{\theta})} \tag{1.3.8}$$

and if we write the direct correlation function as

$$\begin{aligned} c(\underline{s}) &= c_j \quad , \ \underline{s} \in \Gamma_j \\ c(\underline{0}) &= c_0 \end{aligned} \tag{1.3.9}$$

assuming $c(\underline{s})$ takes the same value for all neighbours of order j, then its Fourier expansion becomes

$$\tilde{c}(\underline{\theta}) = c_0 + \sum_{j=1} l_j c_j \lambda_j(\underline{\theta}) . \tag{1.3.10}$$

$\tilde{h}(\underline{\theta})$ takes the form

$$\tilde{h}(\underline{\theta}) = \frac{1}{\rho}\left[\frac{1}{1-\rho[c_0+\sum_{j=1} l_j c_j \lambda_j(\underline{\theta})]} - 1\right] \tag{1.3.11}$$

or, by setting

$$z_j = \frac{\rho l_j c_j}{1-\rho c_0} \tag{1.3.12}$$

with the help of equation (1.2.14) we obtain

$$\tilde{h}(\underline{\theta}) = \frac{1}{\rho}\left[\frac{1}{(1-\rho c_0)(1-\tilde{z}(\underline{\theta}))} - 1\right]$$

$$= \frac{1}{\rho}\left[\frac{U(\underline{\theta};z)}{1-\rho c_0} - 1\right] . \tag{1.3.13}$$

The inverse Fourier transformation of the expression above gives:

$$h(\underline{s}) = \frac{1}{\rho}\left[\frac{P(\underline{s};z)}{1-\rho c_0} - \delta_{\underline{s},\underline{o}}\right] . \tag{1.3.14}$$

We assume the potential function to exclude multiple occupancy of sites; then the pair distribution function vanishes for $\underline{s} = \underline{o}$, and thus

$$c_0 = \frac{1}{\rho}\left[1 - \frac{P(\underline{o};z)}{1-\rho}\right] ; \tag{1.3.15}$$

this, together with equation (1.2.26) gives

$$h(\underline{s}) = \frac{1-\rho}{\rho} F(\underline{s};z) \quad , \quad \underline{s} \neq \underline{o} . \tag{1.3.16}$$

To complete the specification of the correlation functions we add to (1.3.15) the relations obtained from (1.3.12), namely

$$c_j = \frac{z_j P(0;z)}{\ell_j \rho(1-\rho)} \quad . \tag{1.3.17}$$

Finally, by inverting the Fourier expansion (1.3.10), we observe that the direct correlation function outside the origin can be written as

$$c(\underline{s}) = \sum_{j=1} \ell_j e_j p_j(\underline{s}) \quad , \quad \underline{s} \neq \underline{0} \tag{1.3.18}$$

or, with the help of equation (1.3.17), as

$$c(\underline{s}) = \frac{P(0;z)}{\rho(1-\rho)} \sum_{j=1} z_j p_j(\underline{s}) \quad , \quad \underline{s} \neq \underline{0} \quad . \tag{1.3.19}$$

It can be noted that $c(\underline{s})$ is directly related to $p_j(\underline{s})$, the probability of a step from the origin to $\underline{s}$.

From the above, we see that both the direct and total pair correlation functions have simple interpretations in terms of random-walk concepts. The total correlation function $h(\underline{s})$ is given by the first-passage-time probability of random walks starting at the origin and ending at $\underline{s}$, whereas the direct correlation function $c(\underline{s})$ is more simply expressed in terms of the basic probability of walks that start and end at the origin.

It follows that thermodynamic properties of the lattice gas may also be represented in terms of random-walk functions. Thus, the isothermal compressibility, for instance, which is given by

$$K = \beta \rho^{-1} \left[1 - \rho \sum_{\underline{s}} c(\underline{s}) \right]^{-1}$$

$$= \beta \rho^{-1} \left[1 - \rho \tilde{c}(0) \right]^{-1}, \tag{1.3.20}$$

becomes

$$K = \beta(1-\rho)\left[\rho P(\underline{0};z)\left(1-\sum_j z_j\right)\right]^{-1} \qquad (1.3.21)$$

or, if use is made of equation (1.2.26)

$$K = \beta(1-\rho)\left[1-F(\underline{0};z)\right]\left[\rho\left(1-\sum_j z_j\right)\right]^{-1} . \qquad (1.3.22)$$

As outlined before, knowledge of $c(\underline{s})$ or $h(\underline{s})$ for a given density ρ (and a given temperature T) of the system enables us to describe a particular equilibrium state for the lattice gas. The weight function $z(\underline{s})$ for this state can then be evaluated either through equation (1.3.17) or by means of equation (1.3.16). By reversing the argument we can say that knowledge of the weight function $z(\underline{s})$ for every possible density ρ (and temperature T) of the system is sufficient for the evaluation of the thermodynamic properties for all equilibrium states of the system.

We can rephrase the resolution of the lattice-gas problem as follows :

The potential function, and the geometry of the lattice, determine the set of functions $\rho_j(\underline{s})$ and structure functions $\lambda_j(\underline{\alpha})$. The potential also sets the values for the weight factors z_j for each state of the system. We have now the lattice Green's function $P(\underline{s};z)$ for a particular lattice gas model, and through equations

$$\rho(1-\rho)c(\underline{s}) = \frac{z_j}{\rho_j} P(\underline{0};z) \qquad (1.3.23)$$

and

$$\frac{\rho}{1-\rho} h(\underline{s}) = F(\underline{s};z)$$

thermodynamic properties follow.

Unfortunately, we have not been able to divorce the evaluation of all acceptable weight functions $z(\underline{s})$, for a given potential

function $\phi(\underline{s})$, from any reference to the density ρ of the system. However, one can visualize the potential function admitting only a particular set of weight functions, and therefore, make the statement (parallel to that given for the correlation functions) that knowledge of the lattice Green's function, for all weight functions acceptable to a particular potential, is sufficient, in principle, to yield a solution to the lattice gas problem.

From this point of view, it can be said that, the interaction between particles in the system undergoes averaging through random-walk process before it can yield the correlations or the thermodynamic properties.

The relationship that exists between the lattice Green's function and the pair correlations has been exhibited, directly or indirectly, by a number of authors[1-5,9], but none of them - except Joyce in his study of the spherical model of a ferromagnet[5] - seems to have interpreted this relationship in connection with random-walk processes. Stell and Theumann[9] considered the Green's function as an alternative potential function for the system. This interpretation was probably due to the fact that they were working with the mean-spherical approximation, i.e.:

$$C(\underline{s}) = -\beta\phi(\underline{s}) \quad , \underline{s} \neq \underline{o} \quad \text{for all } \rho \qquad (1.3.24)$$

for this, with the equation (1.3.23), reads

$$-\beta\phi(\underline{s}) = \frac{z_j}{\ell_j \rho(1-\rho)} P(\underline{o};\underline{s}) \quad , \underline{s} \neq \underline{o} \; . \qquad (1.3.25)$$

On the other hand, random-walk terminology has been employed previously in connection with the cluster expansions of the Ising model[10,11]. Random-walk concepts proved to be useful in the study of

the combinatorial problem that replaces the evaluation of the cluster sums, and, for this particular purpose, the properties of self-avoiding random-walks became relevant. We note that these are non-Markovian in character as opposed to the class of walks considered here[10]. We do not make any formal attempt to discuss cluster expansions in terms of the lattice Green's function.

The link established between the pair correlation function $h(\underline{r})$ and the lattice Green's function $P(\underline{r},\underline{r})$ may lead to some computational advantage when working with some equations involving multiple-particle correlation functions. For instance, convolution-type integral equations analogous to the OZ relation (1.3.3) and involving multiple-particle correlation functions, have been obtained by functional differentiation methods[12,13]. A considerable number of integrals (or graphs) are eliminated when h-bonds are replaced, according to equation (1.3.14), by P-bonds.

1.4 ORNSTEIN-ZERNIKE SYSTEMS. THE PERCUS-YEVICK APPROXIMATION.

Exact analytical evaluation of the thermodynamic properties for the lattice gas, by means of the pair correlation functions, is a difficult task. It has not been possible to carry out this task, except for some one-dimensional models[14]. The complex structure of the problem leads naturally to the employment of mathematical approximations to overcome the technical difficulties.

Of the various approximations that have been proposed for the pair correlation functions, we shall be primarily concerned with the so-called Ornstein-Zernike assumption[15], which can be stated briefly as follows:

The direct correlation function $C(\underline{s})$ is to behave like $-\beta\phi(\underline{s})$ for $\underline{s}$ such that $\beta\phi(\underline{s}) \ll 1$; in particular $C(\underline{s}) \approx 0$ for $|\underline{s}| > S$, if $\phi(\underline{s}) = 0$ for $|\underline{s}| > S$.

Systems satisfying this condition are called Ornstein-Zernike (OZ) systems. A number of important approximations, such as the Percus-Yevick (PY) approximation (which we shall be also employing) and the mean-spherical (MS) approximation satisfy the OZ condition.

Since we consider only short-ranged potential functions, the employment of the OZ condition implies a short-ranged direct correlation function. Furthermore, for any potential function with a hard core of diameter, S_0 , the requirement that $g(\underline{s})$ vanishes inside the core, completely determines $C(\underline{s})$ for $|\underline{s}| \leq S_0$ when $C(\underline{s})$ is given for $|\underline{s}| > S_0$, as one can observe from equations (1.3.15), (1.3.16) and (1.3.17). For lattice gases interacting only by means of a hard core it is not necessary to make any other assumption in order to evaluate the correlation functions. However, this is not the case when the potential has a soft repulsion or an attractive tail in

addition to the hard core. For these we employ the PY approximation.

The Percus-Yevick approximation supplements the OZ relation (equation (1.3.3)) with the relation

$$c(\underline{\underline{r}}) = \left[1 - e^{(\beta\phi(\underline{\underline{r}})}\right]\left[h(\underline{\underline{r}}) + 1\right] . \qquad (1.4.1)$$

We give here no account of the derivation[16,17] of this approximate relation. We recall, however, that it can be interpreted in terms of graph theory. The omission of a certain class of graphs in the density (or cluster) expansions of either the total or the direct correlation function gives us equation (1.4.1). The PY direct correlation function includes only the graphs (connected, simple and with no articulation points) that have an f-bond between the base points 1 and 2 where $c(\underline{\underline{r}}_2 - \underline{\underline{r}}_1) = c(\underline{\underline{r}})$ [18].

For a potential function given by

$$\begin{aligned}
&\phi(\underline{\underline{r}}) = \infty \quad \text{for} \quad \underline{\underline{r}} = \underline{\underline{0}} \\
&\phi(\underline{\underline{r}}) = \infty \quad \text{for} \quad \underline{\underline{r}} \in \Gamma_j \;, \; 1 \leq j \leq m_0 , \\
&\phi(\underline{\underline{r}}) \neq 0 \quad \text{for} \quad \underline{\underline{r}} \in \Gamma_j \;, \; m_0 + 1 \leq j < m , \\
&\phi(\underline{\underline{r}}) = 0 \quad \text{for} \quad \underline{\underline{r}} \in \Gamma_j \;, \qquad j > m ,
\end{aligned} \qquad (1.4.2)$$

the PY approximation implies that only walks involving steps up to order m are to be considered in the lattice Green's function. The weight function $z(\underline{\underline{r}})$ is given as a function of the lattice gas density ρ, by the system of equations:

$$-\frac{\rho}{1-\rho} = F(\underline{\underline{r}}_j; z) \;, \quad \underline{\underline{r}} \in \Gamma_j \;, \; 1 \leq j \leq m_0 , \qquad (1.4.3)$$

$$\left[1 - e^{(\beta\phi(\underline{\underline{r}})}\right]^{-1} \frac{z_j P(\underline{\underline{0}}; z)}{\ell_j \rho (1-\rho)} - 1 =$$

$$\frac{1-\rho}{\rho} F(\underline{\underline{r}}; z) \;, \; \underline{\underline{r}} \in \Gamma_j \;, \; m_0 + 1 \leq j \leq m . \qquad (1.4.4.)$$

It is a well known fact that, although the direct correlation function tends to zero with increasing $|\underline{s}|$ much more rapidly than the total correlation function, $C(\underline{s})$ has not the range of the potential function[18]. So that, at least some of the graphs omitted in the PY approximation should be accounted for by walks with steps extending beyond the range of $\phi(\underline{s})$. An evaluation of the extent to which these walks contribute to $P(\underline{s},z)$ (and related quantities) for the square lattice gas with first-neighbour exclusion is given in Chapter 2.

We call attention to the possibility of assessing the different approximations for the correlation functions, not only in terms of a class of graphs in the corresponding cluster expansion, but also, in terms of the types of walks involved in the lattice Green's function.

1.5 ORDERED PHASES AND THE INHOMOGENEOUS LATTICE GAS

A common feature displayed by most two-and-three-dimensional lattice gases is the occurrence of phase transitions. These can be of the fluid-fluid type between two disordered phases of the system, or of the solid-fluid type between an ordered and a disordered phase, with the former appearing at higher densities. The first type of transition occurs when the potential function has an attractive tail[11], the second when the potential is a purely repulsive one[19]. Here, we are interested in the study of the latter type of transition. A lattice gas exhibiting both types of transition can be constructed when a proper balance is made of the repulsive and attractive portions of the potential function[20].

A useful framework in which to study the existence of ordered phases of square-type lattice gases with a hard core extending only to nearest neighbours is the following[2]: the lattice is divided into two interwoven sublattices I and II, each site of type I having sites of type II as its nearest neighbours and viceversa. For an ordered phase, the sublattice densities ρ_1 and ρ_2 take different values, since as close packing is approached occupation of one sublattice is favoured. Two interwoven sublattice gases of densities $\rho_1 \neq \rho_2$ represent an ordered phase, of density $\rho = \frac{\rho_1+\rho_2}{2}$, if they are in equilibrium with each other, i.e. if they have the same activities. We call the two-sublattice gas system the inhomogeneous lattice gas.

For lattice gases with hard cores extending beyond nearest neighbours we have to introduce more sublattices; a square lattice gas with nearest and next-to-nearest neighbours interactions would have to be studied within a four-sublattice framework. Although all of the

equations that follow in this and the following section can be readily generalised for any number of sublattices, the fact that we need an approximation such as the Percus-Yevick together with the increased computing time, make it necessary to restrict ourselves to the two-sublattice framework.

For the inhomogeneous lattice gas, the pair correlation functions become 2x2 matrices $[h^{(\alpha\beta)}]$ and $[c^{(\alpha\beta)}]$, each matrix element depending only on the species α and β and on the relative position $\underline{s}$ of the two sites involved. The one-body distribution function takes two values ρ_1 and ρ_2, the sublattice densities.

The Fourier expansions of the correlations are:

$$\tilde{h}^{(\alpha\beta)}(\underline{q}) = \sum_{\underline{s}} h^{(\alpha\beta)}(\underline{s})\, e^{i\underline{s}\cdot\underline{q}} \tag{1.5.1}$$

and

$$\tilde{c}^{(\alpha\beta)}(\underline{q}) = \sum_{\underline{s}} c^{(\alpha\beta)}(\underline{s})\, e^{i\underline{s}\cdot\underline{q}} , \tag{1.5.2}$$

so that the equivalent OZ relation in $\underline{q}$-space is

$$\tilde{h}^{(\alpha\beta)}(\underline{q}) = \tilde{c}^{(\alpha\beta)}(\underline{q}) + \sum_{\epsilon=1}^{2} \tilde{h}^{(\alpha\epsilon)}(\underline{q})\, \rho_\epsilon\, \tilde{c}^{(\epsilon\beta)}(\underline{q}) , \tag{1.5.3}$$

which if solved for $\tilde{h}^{(\alpha\beta)}$, gives:

$$\begin{aligned}
\tilde{h}^{(11)}(\underline{q}) &= \left[\tilde{c}^{(11)}(1-\rho_2\tilde{c}^{(22)}) + \rho_2\,\tilde{c}^{(12)}\tilde{c}^{(21)}\right]\Delta^{-1} \\
\tilde{h}^{(12)}(\underline{q}) &= \tilde{c}^{(12)}\Delta^{-1} \\
\tilde{h}^{(22)}(\underline{q}) &= \left[\tilde{c}^{(22)}(1-\rho_1\tilde{c}^{(11)}) + \rho_1\,\tilde{c}^{(21)}\tilde{c}^{(12)}\right]\Delta^{-1} \\
\tilde{h}^{(21)}(\underline{q}) &= \tilde{c}^{(21)}\Delta^{-1} ,
\end{aligned} \tag{1.5.4}$$

where

$$\Delta = (1-\rho_1\tilde{c}^{(11)})(1-\rho_2\tilde{c}^{(22)}) - \rho_1\rho_2\,\tilde{c}^{(12)}\tilde{c}^{(21)} .$$

If we write

$$
\begin{aligned}
c_0^{(1)} &= c^{(11)}(\underline{0}) \ , \\
c_0^{(2)} &= c^{(22)}(\underline{0}) \ , \\
c_j^{(1)} &= c^{(11)}(\underline{s}) \qquad \text{for } \underline{s} \in \Gamma_j \ , \\
c_j^{(2)} &= c^{(22)}(\underline{s}) \qquad \text{for } \underline{s} \in \Gamma_j \ , \\
c_j^{(3)} &= c^{(12)}(\underline{s}) = c^{(21)}(\underline{s}) \qquad \text{for } \underline{s} \in \Gamma_j
\end{aligned}
\tag{1.5.5}
$$

for the direct correlation function, its Fourier expansion takes the form

$$
\begin{aligned}
\tilde{c}^{(11)}(\underline{\theta}) &= c_0^{(1)} + \sum_j \rho_j c_j^{(1)} \lambda_j(\underline{\theta}) \\
\tilde{c}^{(22)}(\underline{\theta}) &= c_0^{(2)} + \sum_j \rho_j c_j^{(2)} \lambda_j(\underline{\theta}) \\
\tilde{c}^{(12)}(\underline{\theta}) &= \tilde{c}^{(21)}(\underline{\theta}) = \sum_j \rho_j c_j^{(3)} \lambda_j(\underline{\theta}) \ .
\end{aligned}
\tag{1.5.6}
$$

The orders j should be compatible with the types of sites in the definitions (1.5.5).

The Fourier expansions $\tilde{h}^{(\alpha\beta)}$ take now the form:

$$
\tilde{h}^{(11)}(\underline{\theta}) = \frac{1}{\rho_1}\left[\frac{1-\sum_j z_j^{(2)}\lambda_j}{(1-\sum_j z_j^{(1)}\lambda_j)(1-\sum_j z_j^{(2)}\lambda_j)-\left[\sum_j z_j^{(3)}\lambda_j\right]^2} - 1\right] \tag{1.5.7}
$$

$$
\tilde{h}^{(22)}(\underline{\theta}) = \frac{1}{\rho_2}\left[\frac{1-\sum_j z_j^{(1)}\lambda_j}{(1-\sum_j z_j^{(1)}\lambda_j)(1-\sum_j z_j^{(2)}\lambda_j)-\left[\sum_j z_j^{(3)}\lambda_j\right]^2} - 1\right] \tag{1.5.8}
$$

$$
\tilde{h}^{(12)}(\underline{\theta}) = \tilde{h}^{(21)}(\underline{\theta}) = \left[\rho_1\rho_2(1-\rho_1 c_0^{(1)})(1-\rho_2 c_0^{(2)})\right]^{-\frac{1}{2}} \times
$$

$$
\times \frac{\sum_j z_j^{(3)}\lambda_j}{(1-\sum_j z_j^{(1)}\lambda_j)(1-\sum_j z_j^{(2)}\lambda_j)-\left[\sum_j z_j^{(3)}\lambda_j\right]^2} \ , \tag{1.5.9}
$$

where the inhomogeneous weights $z_j^{(1)}$, $z_j^{(2)}$ and $z_j^{(3)}$ are defined by

$$z_j^{(1)} = \frac{\ell_j \rho_1 c_j^{(1)}}{1-\rho_1 c_o^{(1)}} \quad ,$$

$$z_j^{(2)} = \frac{\ell_j \rho_2 c_j^{(2)}}{1-\rho_2 c_o^{(2)}} \qquad (1.5.10)$$

and

$$z_j^{(3)} = \left[\frac{\rho_1 \rho_2}{(1-\rho_1 c_o^{(1)})(1-\rho_2 c_o^{(2)})}\right]^{\frac{1}{2}} \ell_j c_j^{(3)} \quad .$$

We further define weight functions $z^{(1)}$, $z^{(2)}$ and $z^{(3)}$ by

$$z^{(1)}(\underline{s}) = \ell_j^{-1} z_j^{(1)} \quad , \quad \underline{s} \in \Gamma_j \, ,$$

$$z^{(2)}(\underline{s}) = \ell_j^{-1} z_j^{(2)} \quad , \quad \underline{s} \in \Gamma_j \, ,$$

$$z^{(3)}(\underline{s}) = \ell_j^{-1} z_j^{(3)} \quad , \quad \underline{s} \in \Gamma_j \, ,$$

$$z^{(1)}(\underline{o}) = z^{(2)}(\underline{o}) = z^{(3)}(\underline{o}) = 0 \, , \qquad (1.5.11)$$

and recall the properties of the structure functions λ_j (see equation (1.2.20)), to note that the expression $\sum_j z_j^{(n)} \lambda_j$ is the Fourier expansion $\tilde{z}^{(n)}(\underline{\theta})$ of the weight function $z^{(n)}(\underline{s})$. We can now introduce the inhomogeneous lattice Green's functions, and proceed to specify the pair correlations in terms of random-walk concepts. The Green's functions may be written as:

$$P^{(1)}(\underline{s}; z^{(1)}, z^{(2)}, z^{(3)}) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int U^{(1)} e^{-i\underline{s}\cdot\underline{\theta}} d\underline{\theta} \, ,$$

$$P^{(2)}(\underline{s}; z^{(1)}, z^{(2)}, z^{(3)}) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int U^{(2)} e^{-i\underline{s}\cdot\underline{\theta}} d\underline{\theta} \, , \qquad (1.5.12)$$

$$P^{(3)}(\underline{s}; z^{(1)}, z^{(2)}, z^{(3)}) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int U^{(3)} e^{-i\underline{s}\cdot\underline{\theta}} d\underline{\theta}$$

where

$$U^{(1)} = \frac{1-\tilde{z}^{(2)}}{(1-\tilde{z}^{(1)})(1-\tilde{z}^{(2)}) - (\tilde{z}^{(3)})^2} \, ,$$

$$U^{(2)} = \frac{1-\tilde{z}^{(1)}}{(1-\tilde{z}^{(1)})(1-\tilde{z}^{(2)}) - (\tilde{z}^{(3)})^2} \, ,$$

$$U^{(3)} = \frac{\tilde{z}^{(3)}}{(1-\tilde{z}^{(1)})(1-\tilde{z}^{(2)}) - (\tilde{z}^{(3)})^2} \, . \qquad (1.5.13)$$

The total correlation function $h^{(\alpha\beta)}$ is then related to the above as follows:

$$h^{(11)}(\underline{\ell}) = \frac{1}{\rho_1}\left[\frac{P^{(1)}(\underline{\ell};z^{(1)},z^{(2)},z^{(3)})}{1-\rho_1 c_0^{(1)}} - \delta_{\underline{\ell},\underline{0}}\right], \quad (1.5.14)$$

$$h^{(22)}(\underline{\ell}) = \frac{1}{\rho_2}\left[\frac{P^{(2)}(\underline{\ell};z^{(1)},z^{(2)},z^{(3)})}{1-\rho_2 c_0^{(2)}} - \delta_{\underline{\ell},\underline{0}}\right] \quad (1.5.15)$$

and

$$h^{(12)}(\underline{\ell}) = h^{(21)}(\underline{\ell}) = \left[\rho_1\rho_2(1-\rho_1 c_0^{(1)})(1-\rho_2 c_0^{(2)})\right]^{-\frac{1}{2}} \times P^{(3)}(\underline{\ell};z^{(1)},z^{(2)},z^{(3)}). \quad (1.5.16)$$

Since there is no multiple occupancy of sites, we have:

$$c_0^{(1)} = \frac{1}{\rho_1}\left[1 - \frac{P^{(1)}(\underline{0};z^{(1)},z^{(2)},z^{(3)})}{1-\rho_1}\right] \quad (1.5.17)$$

and

$$c_0^{(2)} = \frac{1}{\rho_2}\left[1 - \frac{P^{(2)}(\underline{0},z^{(1)},z^{(2)},z^{(3)})}{1-\rho_2}\right]. \quad (1.5.18)$$

These, together with (1.5.10), give the direct correlation for $\underline{\ell} \neq \underline{0}$ in terms of lattice Green's functions, namely

$$c_j^{(1)} = \frac{z_j^{(1)} P^{(1)}(\underline{0};z^{(1)},z^{(2)},z^{(3)})}{\ell_j \rho_1 (1-\rho_1)}, \quad (1.5.19)$$

$$c_j^{(2)} = \frac{z_j^{(2)} P^{(2)}(\underline{0};z^{(1)},z^{(2)},z^{(3)})}{\ell_j \rho_2 (1-\rho_2)} \quad (1.5.20)$$

and

$$c_j^{(3)} = \frac{z_j^{(3)}}{\ell_j}\left[\frac{P^{(1)}(\underline{0};z^{(1)},z^{(2)},z^{(3)})\,P^{(2)}(\underline{0};z^{(1)},z^{(2)},z^{(3)})}{\rho_1(1-\rho_1)\rho_2(1-\rho_2)}\right]^{\frac{1}{2}}. \quad (1.5.21)$$

Finally, the total correlation function can be written as

$$h^{(11)}(\underline{\ell}) = \frac{1-\rho_1}{\rho_1} F^{(1)}(\underline{\ell};z^{(1)},z^{(2)},z^{(3)}), \quad \underline{\ell} \neq \underline{0}, \quad (1.5.22)$$

$$h^{(22)}(\underline{z}) = \frac{1-\rho_2}{\rho_2} F^{(2)}(\underline{z}; z^{(1)}, z^{(2)}, z^{(3)}) , \quad \underline{z} \neq \underline{0} \qquad (1.5.23)$$

and

$$h^{(12)}(\underline{z}) = h^{(21)}(\underline{z}) = \left[\frac{(1-\rho_1)(1-\rho_2)}{\rho_1 \rho_2} \right]^{\frac{1}{2}} \times$$
$$\times F^{(3)}(\underline{z}; z^{(1)}, z^{(2)}, z^{(3)}) \qquad (1.5.24)$$

where

$$F^{(1)}(\underline{z}; z^{(1)}, z^{(2)}, z^{(3)}) = \frac{P^{(1)}(\underline{z}; z^{(1)}, z^{(2)}, z^{(3)}) - \delta_{\underline{z},\underline{0}}}{P^{(1)}(\underline{0}; z^{(1)}, z^{(2)}, z^{(3)})} ,$$
$$F^{(2)}(\underline{z}; z^{(1)}, z^{(2)}, z^{(3)}) = \frac{P^{(2)}(\underline{z}; z^{(1)}, z^{(2)}, z^{(3)}) - \delta_{\underline{z},\underline{0}}}{P^{(2)}(\underline{0}; z^{(1)}, z^{(2)}, z^{(2)})} \qquad (1.5.25)$$

and

$$F^{(3)}(\underline{z}; z^{(1)}, z^{(2)}, z^{(3)}) = \frac{P^{(3)}(\underline{z}; z^{(1)}, z^{(2)}, z^{(3)})}{\left[P^{(1)}(\underline{0}; z^{(1)}, z^{(2)}, z^{(3)}) P^{(2)}(\underline{0}; z^{(1)}, z^{(2)}, z^{(3)}) \right]^{\frac{1}{2}}} , \quad \underline{z} \neq \underline{0} .$$

Equations (1.5.25) define the first-passage-time generating functions in terms of the lattice Green's functions.

For a potential function as in (1.4.2) employment of the PY approximation permits us to obtain the weight functions $z^{(1)}$, $z^{(2)}$ and $z^{(3)}$, as the functions of the densities ρ_1 and ρ_2, by solving the system of equations:

$$\frac{\rho_1}{1-\rho_1} = F^{(1)} ,$$
$$\frac{\rho_2}{1-\rho_2} = F^{(2)} , \qquad (1.5.26)$$
$$\left[\frac{\rho_1 \rho_2}{(1-\rho_1)(1-\rho_2)} \right]^{\frac{1}{2}} = F^{(3)} , \quad \text{for} \quad 1 \leq j \leq m_0$$

and

$$\left(1 - e^{\beta \phi(\underline{z})}\right)^{-1} c_j^{(1)} - 1 = \frac{1-\rho_1}{\rho_1} F^{(1)} ,$$
$$\left(1 - e^{\beta \phi(\underline{z})}\right)^{-1} c_j^{(2)} - 1 = \frac{1-\rho_2}{\rho_2} F^{(2)} , \qquad (1.5.27)$$

$$(1-e^{\beta\phi(\underline{x})})^{-1}c_j^{(3)} - 1 = \left[\frac{(1-\rho_1)(1-\rho_2)}{\rho_1\rho_2}\right]^{\frac{1}{2}} F^{(3)},$$

for $M_0+1 \leq j \leq m$, with $c_j^{(1)}$, $c_j^{(2)}$ and $c_j^{(3)}$ given by (1.5.19), (1.5.20) and (1.5.21), respectively.

Thermodynamic properties can be obtained through the inhomogeneous analogues of equations (1.3.9) and (1.3.5), i.e.:

$$\beta\frac{\partial P}{\partial \rho} = \left\{1 + \frac{1}{\rho_1+\rho_2}\left[\rho_1^2 \tilde{h}^{(11)}(\underline{0}) + \rho_2^2 \tilde{h}^{(22)}(\underline{0}) + 2\rho_1\rho_2 \tilde{h}^{(12)}(\underline{0})\right]\right\}^{-1} \quad (1.3.28)$$

and

$$\beta\frac{\partial P}{\partial \rho} = 1 - \frac{1}{\rho_1+\rho_2}\left[\rho_1^2 \tilde{c}^{(11)}(\underline{0}) + \rho_2^2 \tilde{c}^{(22)}(\underline{0}) + 2\rho_1\rho_2 \tilde{c}^{(12)}(\underline{0})\right] \quad (1.3.29)$$

where $\rho = \frac{\rho_1+\rho_2}{2}$.

All expressions derived so far in this section must reduce to the equivalent homogeneous expressions if we set $\rho_1 = \rho_2$ and $c_j^{(1)} = c_j^{(2)}$ (also $c_0^{(1)} = c_0^{(2)}$), for this implies a disordered phase. We show here that this is the case for k-dimensional cubic lattice gases. We first note, from equation (1.5.10) that $\rho_1 = \rho_2$ and $c_j^{(1)} = c_j^{(2)}$ implies $\tilde{z}^{(1)} = \tilde{z}^{(2)}$, and therefore

$$U^{(1)} = U^{(2)} = \frac{1 - \tilde{z}^{(1)}}{(1-\tilde{z}^{(1)})^2 - (\tilde{z}^{(3)})^2}$$

$$= \frac{1}{2}\left[\frac{1}{1-\tilde{z}^{(1)}-\tilde{z}^{(3)}} + \frac{1}{1-\tilde{z}^{(1)}+\tilde{z}^{(3)}}\right] \quad (1.5.30)$$

and

$$U^{(3)} = \frac{\tilde{z}^{(3)}}{(1-\tilde{z}^{(1)})^2 - (\tilde{z}^{(3)})^2}$$

$$= \frac{1}{2}\left[\frac{1}{1-\tilde{z}^{(1)}-\tilde{z}^{(3)}} - \frac{1}{1-\tilde{z}^{(1)}+\tilde{z}^{(3)}}\right]. \quad (1.5.31)$$

Now, for the cubic lattices Fourier expansions are

cosine expansions, and, by writing $\underline{s} = (s_1, \cdots, s_k)$ we observe that the structure functions λ_j have the form

$$\lambda_j(\underline{\theta}) = \sum \prod_{i=1}^{k} \cos s_i \theta_i \,, \tag{1.5.32}$$

where $\sum_i^k s_i$ is an even number for those λ_j in $\mathcal{Z}^{(1)}$ and $\mathcal{Z}^{(2)}$, whereas $\sum_i^k s_i$ is odd for those λ_j in $\mathcal{Z}^{(3)}$.

Thus

$$\int_{-\pi}^{\pi} \cdots \int \frac{\prod_{i=1}^{k} \cos s_i \theta_i \, d\underline{\theta}}{1 - \underline{z}^{(1)} - \underline{z}^{(3)}} =$$

$$\int_{-\pi}^{\pi} \cdots \int \frac{\prod_{i=1}^{k} \cos s_i \theta_i \, d\underline{\theta}}{1 - \underline{z}^{(1)} + \underline{z}^{(2)}} \,, \quad \sum_{i=1}^{k} s_i \quad \text{even} \tag{1.5.33}$$

and

$$\int_{-\pi}^{\pi} \cdots \int \frac{\prod_{i=1}^{k} \cos s_i \theta_i \, d\underline{\theta}}{1 - z^{(1)} - z^{(3)}} =$$

$$- \int_{-\pi}^{\pi} \cdots \int \frac{\prod_{i=1}^{k} \cos s_i \theta_i \, d\underline{\theta}}{1 - \underline{z}^{(1)} + \underline{z}^{(3)}} \,, \quad \sum_{i=1}^{k} s_i \ \text{odd} \,. \tag{1.5.34}$$

We can therefore write

$$P^{(1)}(\underline{s}; z^{(1)} = z^{(2)}, z^{(3)}) = P^{(2)}(\underline{s}; z^{(1)} = z^{(2)}, z^{(3)}) =$$

$$\frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int \frac{\prod_{i=1}^{k} \cos s_i \theta_i \, d\underline{\theta}}{1 - \underline{z}^{(1)} - \underline{z}^{(3)}} \,, \quad \sum_{i=1}^{k} s_i \quad \text{even} \tag{1.5.35}$$

and

$$P^{(3)}(\underline{s}; z^{(1)} = z^{(2)}, z^{(3)}) =$$

$$\frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int \frac{\prod_{i=1}^{k} \cos s_i \theta_i \, d\underline{\theta}}{1 - z^{(1)} - z^{(3)}} \,, \quad \sum_{i=1}^{k} s_i \ \text{odd} \,. \tag{1.5.36}$$

Finally, since for $z^{(1)} = z^{(2)}$

$$\underline{z}(\underline{\theta}) = \underline{z}^{(1)}(\underline{\theta}) + \underline{z}^{(3)}(\underline{\theta}) \,, \tag{1.5.37}$$

the equivalence of the inhomogeneous and homogeneous lattice Green's functions follows immediately.

For the cubic lattice gases, with the potential functions extending only to nearest neighbours, the inhomogeneous Green's functions reduce to the homogeneous function even for the ordered phase, since for them all the $\mathcal{Z}_j^{(1)}$ and $\mathcal{Z}_j^{(2)}$ vanish, and hence $\mathcal{Z}(\underline{s}) = \mathcal{Z}^{(3)}(\underline{s})$. We shall see in the next chapter that this is also the case for the honeycomb lattice.

1.6 THE ACTIVITY OF THE LATTICE GAS. PARTIALLY COUPLED PAIR-CORRELATION AND RANDOM-WALK FUNCTIONS

As we mentioned in the preceding section, we intend to determine the existence of ordered phases by examining the activities of the sublattice gases. Exact expressions for these, in terms of the pair correlations can be derived when use is made of the concept of a partially coupled particle[2]. That is, if the particle at $\underline{s}_1$ is assumed to be coupled to any other particle at $\underline{s}_i$ through a weakened potential $\xi\phi(\underline{s}_1-\underline{s}_i)$, where ξ is a coupling parameter such that $0\leq\xi\leq 1$, the activity γ for a lattice gas (with no multiple occupancy of sites) is given by[2]:

$$\gamma = \frac{\rho(\underline{s}_1)}{1-\rho(\underline{s}_1)}\exp\left\{\beta\sum_{\underline{s}_i}\phi(\underline{s}_1-\underline{s}_i)\left[\int_0^1 g(\underline{s}_1-\underline{s}_i;\xi)\,d\xi\right]\rho(\underline{s}_i)\right\} \qquad (1.6.1)$$

where $g(\underline{s};\xi)$ is the partially-coupled pair distribution function.

Here, we derive expressions for $h(\underline{s};\xi)=g(\underline{s};\xi)-1$, the partially-coupled total correlation function, in terms of the appropriate random-walk functions. The procedure is similar to that employed in the preceding section for the fully coupled correlations.

The OZ relation in $\underline{\omega}$-space is now assumed[2] to be

$$\tilde{h}^{(\alpha\beta)}(\underline{\omega};\xi) = \tilde{c}^{(\alpha\beta)}(\underline{\omega};\xi) + \sum_{\epsilon=1}^{2}\tilde{h}^{(\alpha\epsilon)}(\underline{\omega};\xi)\rho_\epsilon\tilde{c}^{(\epsilon\beta)}(\underline{\omega}), \qquad (1.6.2)$$

or, if solved for $h^{(\alpha\beta)}$,

$$\tilde{h}^{(11)}(\underline{\omega};\xi) = \left[\tilde{c}^{(11)}(\xi)(1-\rho_2\tilde{c}^{(22)}) + \rho_2\tilde{c}^{(12)}(\xi)\tilde{c}^{(21)}\right]\Delta^{-1}$$

$$\tilde{h}^{(12)}(\underline{\omega};\xi) = \left[\tilde{c}^{(12)}(\xi)(1-\rho_1\tilde{c}^{(11)}) + \rho_1\tilde{c}^{(11)}(\xi)\tilde{c}^{(12)}\right]\Delta^{-1}$$

$$\tilde{h}^{(22)}(\underline{\theta};\underline{\xi}) = \left[\tilde{c}^{(22)}(\underline{\xi})(1-\rho_1\tilde{c}^{(11)}) + \rho_1\tilde{c}^{(21)}(\underline{\xi})\tilde{c}^{(12)}\right]\Delta^{-1}$$
$$\tilde{h}^{(21)}(\underline{\theta};\underline{\xi}) = \left[\tilde{c}^{(21)}(\underline{\xi})(1-\rho_2\tilde{c}^{(22)}) + \rho_2\tilde{c}^{(22)}(\underline{\xi})\tilde{c}^{(21)}\right]\Delta^{-1}, \qquad (1.6.3)$$

where Δ is as in (1.5.4). And the Fourier expansion of the partially-coupled direct correlation is:

$$\tilde{c}^{(11)}(\underline{\theta};\underline{\xi}) = c_0^{(1)}(\underline{\xi}) + \sum_j \ell_j c_j^{(1)}(\underline{\xi})\lambda_j(\underline{\theta})$$
$$\tilde{c}^{(22)}(\underline{\theta};\underline{\xi}) = c_0^{(2)}(\underline{\xi}) + \sum_j \ell_j c_j^{(2)}(\underline{\xi})\lambda_j(\underline{\theta}) \qquad (1.6.4)$$
$$\tilde{c}^{(12)}(\underline{\theta};\underline{\xi}) = \tilde{c}^{(21)}(\underline{\theta};\underline{\xi}) = \sum_j \ell_j c_j^{(3)}(\underline{\xi})\lambda_j(\underline{\theta}) .$$

Now, if we define partially-coupled weight factors by:

$$z_j^{(1)}(\underline{\xi}) = \frac{\ell_j \rho_1 c_j^{(1)}(\underline{\xi})}{1-\rho_1 c_0^{(1)}(\underline{\xi})}$$
$$z_j^{(2)}(\underline{\xi}) = \frac{\ell_j \rho_2 c_j^{(2)}(\underline{\xi})}{1-\rho_2 c_0^{(2)}(\underline{\xi})} \qquad (1.6.5)$$

and
$$z_j^{(3)}(\underline{\xi}) = \left[\frac{\rho_1\rho_2}{(1-\rho_1 c_0^{(1)}(\underline{\xi}))(1-\rho_2 c_0^{(2)}(\underline{\xi}))}\right]^{\frac{1}{2}} \ell_j c_j^{(3)}(\underline{\xi})$$

and from these, the corresponding weight functions, $\tilde{z}^{(1)}(\underline{s};\underline{\xi})$, $\tilde{z}^{(2)}(\underline{s};\underline{\xi})$ and $\tilde{z}^{(3)}(\underline{s};\underline{\xi})$, we can introduce the following partially-coupled lattice Green's functions:

$$R^{(1\xi,2)}(\underline{s};\underline{\xi}) = \frac{1}{(2\pi)^k}\int_{-\pi}^{\pi}\cdots\int \frac{(1-\tilde{z}^{(1)}(\underline{\xi}))(1-\tilde{z}^{(2)})}{(1-\tilde{z}^{(1)})(1-\tilde{z}^{(2)}) - (\tilde{z}^{(3)})^2} e^{-i\underline{s}\cdot\underline{\theta}}\, d\underline{\theta},$$

$$R^{(1\xi,3)}(\underline{s};\underline{\xi}) = \frac{1}{(2\pi)^k}\int_{-\pi}^{\pi}\cdots\int \frac{(1-\tilde{z}^{(1)}(\underline{\xi}))\,\tilde{z}^{(3)}}{(1-\tilde{z}^{(1)})(1-\tilde{z}^{(2)}) - (\tilde{z}^{(3)})^2} e^{-i\underline{s}\cdot\underline{\theta}}\, d\underline{\theta},$$

$$R^{(3\xi,1)}(\underline{s};\underline{\xi}) = \frac{1}{(2\pi)^k}\int_{-\pi}^{\pi}\cdots\int \frac{(1-\tilde{z}^{(1)})\,\tilde{z}^{(3)}(\underline{\xi})}{(1-\tilde{z}^{(1)})(1-\tilde{z}^{(2)}) - (\tilde{z}^{(3)})^2} e^{-i\underline{s}\cdot\underline{\theta}}\, d\underline{\theta}, \qquad (1.6.7)$$

$$R^{(3\xi,3)}(\underline{s};\underline{\xi}) = \frac{1}{(2\pi)^k}\int_{-\pi}^{\pi}\cdots\int \frac{\tilde{z}^{(3)}(\underline{\xi})\,\tilde{z}^{(3)}}{(1-\tilde{z}^{(1)})(1-\tilde{z}^{(2)}) - (\tilde{z}^{(3)})^2} e^{-i\underline{s}\cdot\underline{\theta}}\, d\underline{\theta}.$$

Fourier inversion of (1.6.3), after (1.6.4) has been taken into account, gives for $h^{(\alpha\beta)}(\underline{s};\underline{\xi})$ the expressions

$$h^{(11)}(s;\xi) = \frac{1}{\rho_1}\left\{ \frac{P^{(1)}(\underline{s})}{1-\rho_1 c_0^{(1)}} - \frac{1-\rho_1 c_0^{(1)}(\xi)}{1-\rho_1 c_0^{(1)}} R^{(1\xi,2)}(\underline{s};\xi) + \left[\frac{(1-\rho_1 c_0^{(1)}(\xi))(1-\rho_2 c_0^{(2)}(\xi_1))}{(1-\rho_1 c_0^{(1)})(1-\rho_2 c_0^{(2)})}\right]^{\frac{1}{2}} R^{(3\xi,3)}(s;\xi) \right\} \tag{1.6.8}$$

and

$$h^{(12)}(\underline{s};\xi) = \left[\rho_1\rho_2(1-\rho_1 c_0^{(1)})(1-\rho_2 c_0^{(2)})\right]^{-\frac{1}{2}} \left[P^{(3)}(\underline{s}) - (1-\rho_1 c_0^{(1)}(\xi)) R^{(1\xi,3)}(\underline{s};\xi) \right] +$$

$$\left[\rho_1\rho_2(1-\rho_1 c_0^{(1)}(\xi))(1-\rho_2 c_0^{(2)}(\xi))\right]^{\frac{1}{2}} (1-\rho_2 c_0^{(2)})^{-1} R^{(3\xi,1)}(\underline{s};\xi), \tag{1.6.9}$$

where we have written $P^{(h)}(\underline{s})$ instead of $P^{(h)}(\underline{s};z^{(1)},z^{(2)},z^{(3)})$. $h^{(22)}(\underline{s};\xi)$ and $h^{(21)}(\underline{s};\xi)$ can be obtained from equations (1.6.8) and (1.6.9) by interchanging indexes 1 and 2 in these and in equations (1.6.7).

Since we consider that a partially coupled particle still excludes other particles from its own site by an undamped infinite repulsion, we have the following extra relationships:

$$\begin{aligned} 1-\rho_1 c_0^{(1)} &= \frac{P^{(1)}(\underline{0})}{1-\rho_1}, \\ 1-\rho_2 c_0^{(2)} &= \frac{P^{(2)}(\underline{0})}{1-\rho_2}, \\ 1-\rho_1 c_0^{(1)}(\xi) &= \frac{P^{(1)}(\underline{0})}{1-\rho_1}\left\{R^{(1\xi,2)}(\underline{0};\xi)\left[1-\frac{R^{(3\xi,3)}(\underline{0};\xi)}{(R^{(1\xi,2)}(\underline{0};\xi)R^{(2\xi,1)}(\underline{0};\xi))^{\frac{1}{2}}}\right]\right\}^{-1} \end{aligned} \tag{1.6.10}$$

and

$$1-\rho_2 c_0^{(2)}(\xi) = \frac{P^{(2)}(\underline{0})}{1-\rho_2}\left\{R^{(2\xi,1)}(\underline{0};\xi)\left[1-\frac{R^{(3\xi,3)}(\underline{0};\xi)}{(R^{(2\xi,1)}(\underline{0};\xi)R^{(1\xi,2)}(\underline{0};\xi))^{\frac{1}{2}}}\right]\right\}^{-1}$$

It is not difficult to see that, by setting $\xi = 1$ in the above expressions, that is by fully coupling particle one to the system, we recover the equations for the correlation functions given in section 1.5.

And once again, for a potential function as in (1.4.2), employment of the PY approximation allows us to determine the partially-coupled weight functions $\mathbb{Z}^{(n)}(\underline{\underline{s}};\underline{\underline{\xi}})$ as functions of the sublattice densities ρ_1 and ρ_2. The PY approximation, in this case, becomes

$$c^{(\alpha\beta)}(\underline{\underline{s}};\underline{\underline{\xi}}) = \left[1 - e^{\beta\xi\phi(\underline{\underline{s}})}\right]\left[h^{(\alpha\beta)}(\underline{\underline{s}};\underline{\underline{\xi}}) + 1\right] . \qquad (1.6.11)$$

1.7 DECAY OF PAIR CORRELATIONS . ASYMPTOTIC FORMS

In this section we shall be concerned with the properties of the total correlation function at large distances. The study of the asymptotic form of $h(\underline{s})$ acquired new interest after investigations, first by Fisher and Widom [21] and then by Throop and Fisk [22], gained insight into the correlating effects of the repulsive and attractive components of the interparticle potential, on the long range behaviour of $h(\underline{s})$.

Fisher and Widom discussed the decay of $h(s)$ for linear (lattice and continuous) systems. The range of the potential function for the lattice system they considered involved first neighbour exclusion and second and third neighbour attractions. They found that when the attraction is restricted to second nearest sites, the asymptotic form for $h(s)$ is always oscillatory. When attractions extend to third nearest sites the decay of $h(s)$ can be either oscillatory or monotonic depending on the thermodynamic state of the system.

Throop and Fisk considered three-dimensional continuous systems and concluded that it is possible for these to exhibit both oscillatory or monotonic decay, according to the thermodynamic state of the system and provided that the potential function has both repulsive and attractive components. They also argue that the type of decay for $h(\underline{s})$ depends on the signs of the moments of the Fourier expansion of $C(\underline{s})$ (which are defined below). However, they had difficulties extending their calculations to moments of orders higher than four.

Here we present some general results regarding the behaviour of $h(\underline{s})$ for OZ lattice gases with nearest-neighbour interactions. We then proceed to derive asymptotic forms of $h(\underline{s})$, for the

general OZ lattice gas, in terms of both the weight function and the moments of $\tilde{C}(\underline{\varrho})$. We discuss these moments in terms of random-walk variables and establish the relationship between the results and conjectures of Throop and Fisk and our own.

Let us consider a walker that steps only to the nearest-neighbour sites on a lattice, and restrict the discussion to the class of lattices determined by the following condition:

Any two sites can be connected by walks of either i) an even number or ii) an odd number of steps.

Then, if we take one site as the origin, the rest of the sites fall into two groups according to whether (i) or (ii) applies to them. The sites of group (i) have sites of (ii) as nearest-neighbours and vice versa. Examples of this class of lattices are the k-D cubic and the 2-D honeycomb lattices. The 2-D triangular lattice does not fall into this classification.

Consider now a lattice gas with first-neighbour interactions only and treat it as an OZ system. The weight function becomes

$$z(\underline{s}) = \lambda_1^{-1} z_1 \quad , \quad \underline{s} \in \Gamma_1$$
$$z(\underline{s}) = 0 \qquad \text{otherwise} . \tag{1.7.1}$$

And the random-walk functions can be written as follows

$$P_n(\underline{s}; \varrho_1 \ldots \varrho_n) = P_n(\underline{s})$$
$$P_n(\underline{s}; z_1) = P_n(\underline{s}) z_1^n$$
$$P(\underline{s}; z_1) = \sum_n P_n(\underline{s}) z_1^n . \tag{1.7.2}$$

also, from equation (1.2.17), we have

$$P(\underline{o};z_1) - z_1 P(\underline{s};z_1) = 1 \quad , \quad \underline{s} \in \Gamma_1 \quad . \tag{1.7.3}$$

This, together with (1.2.26) and (1.3.16), gives

$$h(\underline{s}) = \frac{1-\rho}{\rho} \; \frac{P(\underline{o};z_1) - 1}{z_1 P(\underline{o};z_1)} \quad , \quad \underline{s} \in \Gamma_1 \quad . \tag{1.7.4}$$

Now, for the above mentioned lattices, $P(\underline{s};z_1)$ is either a series in even powers of z_1, if $\underline{s}$ is a site of group (i), or a series in odd powers of z_1, if $\underline{s}$ is a site of group (ii). Then, since $P(\underline{o};z_1) \geq 1$ ($P_0(\underline{o})=1$), we observe from (1.7.4) that $z_1 \leq 0$ if $h(\underline{s}, \underline{s} \in \Gamma_1) < 0$ and $z_1 \geq 0$ if $h(\underline{s}, \underline{s} \in \Gamma_1) > 0$. And since $h(\underline{s}) = (1-\rho) P(\underline{s};z_1) [\rho P(\underline{o};z_1)]^{-1}$ for all $\underline{s} \neq \underline{o}$, we conclude that $h(\underline{s})$ oscillates when $h(\underline{s}, \underline{s} \in \Gamma_1)$ is negative and $h(\underline{s})$ remains positive and decays monotonically when $h(\underline{s}, \underline{s} \in \Gamma_1)$ is positive. The sign the total correlation function takes at nearest neighbours determines its type of decay. The same can be said about the sign of z_1. Furthermore, since $z_1 = \lambda_1 \rho (1-\rho) [P(\underline{o};z_1)]^{-1} c_1$, we see that the sign of z_1 is also the sign of c_1. The PY and the MS approximations suggest that for this model c_1 is negative if the interaction between nearest neighbours is repulsive, and positive if it is attractive.

We make no attempt to extend the argument to lattice gases with longer-ranged potentials, since the interplay of more than one weight factor complicates the situation. Our results for the linear lattice gas with first and second neighbour exclusion (see

Chapter two) suggest that when the decay of $h(\underline{r})$ is oscillatory, the frequency of these oscillations can be density dependent. This is indeed the case for the continuous hard sphere model [23].

Instead we derive now asymptotic forms for the lattice Green's function and the total correlation function of a lattice gas interacting only through attractive forces of unspecified range. We also obtain the asymptotic forms of these functions for the k-dimensional cubic lattice gas with (i) first neighbour repulsive interactions and (ii) first neighbour repulsive and second neighbour attractive interactions. We shall follow the derivation given by Montroll and Weiss [6] for the particular case $P(\underline{r}; z_1)$, $z_1 \geq 0$.

For a symmetrical walk we can expand the structure function $\lambda_j(\underline{\theta})$ as ($\underline{s} = (s_1, \ldots, s_k)$ and $\underline{\theta} = (\theta_1, \ldots, \theta_k)$):

$$\lambda_j(\underline{\theta}) = 1 - \sum_{l} \Lambda_j^{(2)}(l)\,\theta_l^2 + \sum_{l,m} \Lambda_j^{(4)}(l,m)\,\theta_l^2\theta_m^2 - \sum_{l,m,n} \Lambda_j^{(6)}(l,m,n)\,\theta_l^2\theta_m^2\theta_n^2 + \ldots \tag{1.7.5}$$

where the quantities $\Lambda_j^{(2i)}$ are the moments of order $2i$ of the structure function λ_j, and are given by

$$\begin{aligned}
\Lambda_j^{(2)}(l) &= \frac{1}{2!} \sum_{\underline{s}} s_l^2 P_j(\underline{s}) \\
\Lambda_j^{(4)}(l,m) &= \frac{1}{4!} \sum_{\underline{s}} s_l^2 s_m^2 P_j(\underline{s}) \\
\Lambda_j^{(6)}(l,m,n) &= \frac{1}{6!} \sum_{\underline{s}} s_l^2 s_m^2 s_n^2 P_j(\underline{s}) \\
&\vdots
\end{aligned} \tag{1.7.6}$$

It is clear that all moments $\Lambda_j^{(2i)}$ are positive. The expansion of the complete structure function $\tilde{\underline{Z}}$ is:

$$\tilde{\underline{Z}}(\underline{\theta}) = Z^{(0)} - \sum_{\ell} Z^{(2)}(\ell)\,\theta_\ell^2 + \sum_{\ell,m} Z^{(4)}(\ell,m)\,\theta_\ell^2\theta_m^2 - \sum_{\ell,m,n} Z^{(6)}(\ell,m,n)\,\theta_\ell^2\theta_m^2\theta_n^2 + \cdots , \tag{1.7.7}$$

where the quantities $Z^{(2i)}$ are the moments of order $2i$ of the complete structure function $\tilde{\underline{Z}}$ and are defined by

$$\begin{aligned} Z^{(0)} &= \sum_j z_j \\ Z^{(2)}(\ell) &= \sum_j z_j \Lambda_j^{(2)}(\ell) \\ Z^{(4)}(\ell,m) &= \sum_j z_j \Lambda_j^{(4)}(\ell,m) \\ Z^{(6)}(\ell,m,n) &= \sum_j z_j \Lambda_j^{(6)}(\ell,m,n) \\ &\vdots \end{aligned} \tag{1.7.8}$$

With regard to the signs of the $Z^{(2i)}$, we make the following observations:

Although a rigorous proof has not been produced yet, we shall adopt the common assumption that, for systems with potential functions having both repulsive and attractive components, the direct correlation function is negative inside the range of repulsion and positive further out. This supposition is supported by numerous results on theoretical models (for instance, those studied in the following chapter) and by experimental determinations on real fluids, like argon [24]. Now, if we assume $P(\underline{\rho};z)$ to be always positive (as it is in the case for the nearest-neighbour OZ model discussed above and all other models in chapter two), the

assumption on $\mathcal{C}(\underline{s})$ with equation (1.3.23), implies that z_j is negative if the potential is repulsive at Γ_j and positive if it is attractive at Γ_j. For OZ lattice systems we can conclude that : (i) the $Z^{(2i)}$ are negative for fully repulsive potentials, (ii) the $Z^{(2i)}$ are positive for potentials which exclude multiple occupancy but are attractive otherwise, and (iii) the $Z^{(2i)}$ can be positive or negative, according to the values taken by the weight factors z_j, if the potential has an extended repulsive component plus an attractive tail. If the $2i$-th moment is positive then all higher moments are positive (assuming an attractive tail follows a repulsive core).

The Green's function

$$P(\underline{s};z) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int \frac{e^{-i\underline{s}\cdot\underline{\theta}}}{1 - \tilde{z}(\underline{\theta})} \, d\underline{\theta} \qquad (1.7.9)$$

can be expressed as

$$P(\underline{s};z) = \frac{1}{(2\pi)^k} \int_0^{\infty} e^{-\alpha} d\alpha \int_{-\pi}^{\pi} \cdots \int e^{-i\underline{s}\cdot\underline{\theta}} e^{\alpha \tilde{z}(\underline{\theta})} \, d\underline{\theta} \, . \qquad (1.7.10)$$

When $|\underline{s}|$ is large the main contribution to the $\underline{\theta}$ integration comes from values close to the origin if all moments $Z^{(2i)}$ are positive. For the cubic lattice gases with first neighbour repulsion and second neighbour attraction (or with first neighbour repulsion only) the change of variable $(\theta_1, \ldots, \theta_k) \longrightarrow (\pi - \theta_1, \ldots, \pi - \theta_k)$ in equation (1.7.10) gives

$$P(\underline{s};z) = \frac{(-1)^{s_1+\cdots+s_k}}{(2\pi)^k} \int_0^{\infty} e^{-\alpha} d\alpha \int_{-\pi}^{\pi} \cdots \int e^{-i\underline{s}\cdot\underline{\theta}} e^{\alpha \tilde{z}^*(\underline{\theta})} \, d\underline{\theta}$$

(1.7.11)

where for large $|\underline{s}|$ the main contribution to the $\underline{\theta}$ integration comes from small values of $|\underline{\theta}|$ and where $\underline{\tilde{Z}}^*(\underline{\theta})$ is obtained from $\underline{\tilde{Z}}(\underline{\theta})$ by replacing Z_1 by $|Z_1|$.

Let the moments $Z^{(2i)}$ be all positive. Then, by setting $\varphi_\ell = s_\ell \theta_\ell$, and recalling the expansion (1.7.7), equation (1.7.10) for $P(\underline{s};\underline{z})$ becomes:

$$P(\underline{s};\underline{z}) = \frac{1}{(2\pi)^k}\int_0^\infty e^{-\alpha(1-Z^{(0)})}d\alpha \int_{-\pi s_1}^{\pi s_1}\cdots\int_{-\pi s_k}^{\pi s_k} e^{i(\varphi_1+\cdots+\varphi_k)}\times$$

$$\times e^{-\alpha\sum_\ell Z^{(2)}(\ell)\varphi_\ell^2 s_\ell^{-2}}\left\{1+\alpha\sum_{\ell,m} Z^{(4)}(\ell,m)\left[\varphi_\ell\varphi_m s_\ell^{-1}s_m^{-1}\right]^2 -\right.$$

$$\left.-\alpha\sum_{\ell,m,n} Z^{(6)}(\ell,m,n)\left[\varphi_\ell\varphi_m\varphi_n s_\ell^{-1}s_m^{-1}s_n^{-1}\right]^2+\cdots\right\}\frac{d\varphi_1\cdots d\varphi_k}{s_1\cdots s_k}\,. \qquad (1.7.13)$$

If we extend the limits on the $\underline{\varphi}$ integration to $\pm\infty$ $(s_\ell\to\infty)$ only errors of $O[\exp(-cs_\ell^2)]$ appear.

If we let

$$R_n(a) = \int_{-\infty}^{\infty} e^{i\varphi}e^{-a\varphi^2}\varphi^n\,d\varphi\,, \qquad (1.7.14)$$

then

$$P(\underline{s};\underline{z}) \sim \frac{1}{(2\pi)^k}\int_0^\infty e^{-\alpha(1-\tilde{Z}^{(0)})}d\alpha\left\{\prod_{\nu=1}^{k} R_0(\alpha Z^{(2)}(\nu)s_\nu^{-2})\right\}\times$$

$$\times\left\{1+\alpha\sum_{\ell=1}^{k}\frac{Z^{(4)}(\ell,\ell)}{s_\ell^2}\,\frac{R_4(\alpha Z^{(2)}(\ell)s_\ell^{-2})}{R_0(\alpha Z^{(2)}(\ell)s_\ell^{-2})}\right.$$

$$+\alpha\sum_{l\neq m}\frac{Z^{(4)}_{(l,m)}}{s_l^2 s_m^2}\,\frac{R_2(\alpha Z^{(2)}_{(l)}s_l^{-2})\,R_2(\alpha Z^{(2)}_{(m)}s_m^{-2})}{R_0(\alpha Z^{(2)}_{(l)}s_l^{-2})\,R_0(\alpha Z^{(2)}_{(m)}s_m^{-2})}$$

$$-\alpha\sum_{l=1}^{k}\frac{Z^{(6)}_{(l,l,l)}}{s_l^6}\,\frac{R_6(\alpha Z^{(2)}_{(l)}s_l^{-2})}{R_0(\alpha Z^{(2)}_{(l)}s_l^{-2})}$$

$$-\alpha\sum_{l\neq m}\frac{Z^{(6)}_{(l,l,m)}}{s_l^4 s_m^2}\,\frac{R_4(\alpha Z^{(2)}_{(l)}s_l^{-2})\,R_2(\alpha Z^{(2)}_{(m)}s_m^{-2})}{R_0(\alpha Z^{(2)}_{(l)}s_l^{-2})\,R_0(\alpha Z^{(2)}_{(m)}s_m^{-2})}$$

$$-\alpha\sum_{l\neq m\neq n}\frac{Z^{(6)}_{(l,m,n)}}{s_l^2 s_m^2 s_n^2}\,\frac{R_2(\alpha Z^{(2)}_{(l)}s_l^{-2})\,R_2(\alpha Z^{(2)}_{(m)}s_m^{-2})\,R_2(\alpha Z^{(2)}_{(n)}s_n^{-2})}{R_0(\alpha Z^{(2)}_{(l)}s_l^{-2})\,R_0(\alpha Z^{(2)}_{(m)}s_m^{-2})\,R_0(\alpha Z^{(2)}_{(n)}s_n^{-2})}\Bigg\}$$

$$\times(s_1\cdots s_k)^{-1}.$$

(1.7.15)

Also

$$R_0(a)=\left(\frac{\pi}{a}\right)^{\frac{1}{2}}e^{-\frac{1}{4a}},$$

$$\frac{R_2(a)}{R_0(a)}=\frac{1}{2a}\left(1-\frac{1}{2a}\right),$$

$$\frac{R_4(a)}{R_0(a)}=\frac{1}{(2a)^3}\left(3-\frac{6}{2a}+\frac{1}{(2a)^2}\right),$$

$$\frac{R_6(a)}{R_0(a)}=\frac{1}{(2a)^3}\left(15-\frac{45}{2a}+\frac{15}{(2a)^2}-\frac{1}{(2a)^3}\right).$$

(1.7.16)

Then, if we set

$$T_\mu = \int_0^\infty \alpha^{-\frac{1}{2}\mu} e^{-\alpha(1-Z^{(0)})} e^{-\frac{1}{4\alpha}\sum_{\nu=1}^{k} \frac{S_\nu^2}{Z^{(2)}(\nu)}} d\alpha \qquad (1.7.17)$$

we find

$$P(\underline{s};z) \sim \left[(4\pi)^k \prod_{\nu=1}^{k} Z^{(2)}(\nu)\right]^{-\frac{1}{2}k} \Bigg\{ T_k +$$

$$+ \sum_{l=1}^{k} \frac{Z^{(4)}(l,l)}{4\left[Z^{(2)}(l)\right]^2} \left(3T_{k+2} - 3\frac{s_l^2}{Z^{(2)}(l)} T_{k+4} + \frac{s_l^4}{4\left[Z^{(2)}(l)\right]^2} T_{k+6}\right)$$

$$+ \sum_{l\neq m} \frac{Z^{(4)}(l,m)}{4Z^{(2)}(l)Z^{(2)}(m)} \left(T_{k+2} - \frac{1}{2}\left(\frac{s_l^2}{Z^{(2)}(l)} + \frac{s_m^2}{Z^{(2)}(m)}\right) T_{k+4} + \frac{s_l^2 s_m^2}{4Z^{(2)}(l)Z^{(2)}(m)} T_{k+6}\right)$$

$$- \sum_{l=1}^{k} \frac{Z^{(6)}(l,l,l)}{8\left[Z^{(2)}(l)\right]^3} \left(15T_{k+4} - \frac{45 s_l^2}{2Z^{(2)}(l)} T_{k+6}\right.$$

$$\left. + \frac{15 s_l^4}{4\left[Z^{(2)}(l)\right]^2} T_{k+8} - \frac{s_l^6}{8\left[Z^{(2)}(l)\right]^3} T_{k+10}\right)$$

$$- \sum_{l\neq m} \frac{Z^{(6)}(l,l,m)}{8\left[Z^{(2)}(l)\right]^2 Z^{(2)}(m)} \left(3T_{k+4} - \frac{3}{2}\left(\frac{2s_l^2}{Z^{(2)}(l)} + \frac{s_m^2}{Z^{(2)}(m)}\right) T_{k+6}\right.$$

$$+ \frac{1}{4}\left(\frac{s_l^4}{\left[Z^{(2)}(l)\right]^2} + 6\frac{s_l^2 s_m^2}{Z^{(2)}(l)Z^{(2)}(m)}\right) T_{k+8}$$

$$\left. - \frac{s_l^4 s_m^2}{8\left[Z^{(2)}(l)\right]^2 Z^{(2)}(m)} T_{k+10}\right)$$

$$-\sum_{l\neq m\neq n} \frac{Z^{(0)}(l,m,n)}{8 Z^{(2)}(l) Z^{(2)}(m) Z^{(2)}(n)} \left(T_{k+4} - \frac{1}{2}\left(\frac{s_l^2}{Z^{(2)}(l)} + \frac{s_m^2}{Z^{(2)}(m)} + \frac{s_n^2}{Z^{(2)}(n)} \right) T_{k+6} \right.$$

$$+ \frac{1}{4}\left(\frac{s_l^2 s_m^2}{Z^{(2)}(l) Z^{(2)}(m)} + \frac{s_l^2 s_n^2}{Z^{(2)}(l) Z^{(2)}(n)} + \frac{s_m^2 s_n^2}{Z^{(2)}(m) Z^{(2)}(n)} \right) T_{k+8}$$

$$\left. - \frac{1}{8} \frac{s_l^2 s_m^2 s_n^2}{Z^{(2)}(l) Z^{(2)}(m) Z^{(2)}(n)} T_{k+10} \right) \Bigg\} . \qquad (1.7.18)$$

Provided $1 - Z^{(0)}$ and $\sum_\nu s_\nu^2 (Z^{(2)}(\nu))^{-1} > 0$, the integrals T_μ can be expressed as

$$T_\mu = 2 \left(\frac{z}{|\underline{s}|} \right)^{\frac{1}{2}\mu - 1} \left[Z^{(2)} (1 - Z^{(0)}) \right]^{\frac{1}{4}(\mu-2)} \times$$

$$\times K_{\frac{1}{2}\mu - 1} \left[\left(\frac{1 - Z^{(0)}}{Z^{(2)}} \right)^{\frac{1}{2}} |\underline{s}| \right] \qquad (1.7.19)$$

where $Z^{(2)} = \sum_\nu Z^{(2)}(\nu)$ and K_ν is the ν-th modified Bessel function of the second kind.

For the particular cubic lattice gases we are also considering, the asymptotic form for $P(\underline{s}; z)$ is obtained from the above by multiplying the right-hand-side of equation (1.7.18) by the periodic function $(-1)^{s_1 + \ldots + s_k}$ and by replacing z_i by $|z_i|$.

For a lattice gas with structure functions λ_j of the type (1.7.5), we can expand the function $\rho \tilde{c}(\underline{\Theta})$ (see equation (1.3.10)) as follows:

$$\rho\tilde{c}(\underline{\theta}) = C^{(0)} - \sum_{l} C^{(2)}(l)\,\theta_l^2 + \sum_{l,m} C^{(4)}(l,m)\,\theta_l^2\theta_m^2$$

$$- \sum_{l,m,n} C^{(6)}(l,m,n)\,\theta_l^2\theta_m^2\theta_n^2 + \cdots \qquad (1.7.21)$$

where

$$C^{(0)} = \rho(c_0 + \sum_j l_j c_j)$$

$$C^{(2)}(l) = \rho \sum_j l_j c_j \Lambda_j^{(2)}(l)$$

$$C^{(4)}(l,m) = \rho \sum_j l_j c_j \Lambda_j^{(4)}(l,m)$$

$$C^{(6)}(l,m,n) = \rho \sum_j l_j c_j \Lambda_j^{(6)}(l,m,n)$$

$$\vdots$$

(1.7.22)

The quantities $C^{(2i)}$ are called the moments of order $2i$ of the Fourier expansion of $c(\underline{s})$. They are related to the moments $Z^{(2i)}$ by:

$$C^{(0)} = 1 - \frac{P(Q;z)}{1-\rho}\,(1 - Z^{(0)})$$

$$C^{(2)}(l) = \frac{P(Q;z)}{1-\rho}\,Z^{(2)}(l)$$

(1.7.23)

$$C^{(4)}(\ell,m) = \frac{P(\underline{0};z)}{1-\rho} Z^{(4)}(\ell,m)$$

$$C^{(6)}(\ell,m,n) = \frac{P(\underline{0};z)}{1-\rho} Z^{(6)}(\ell,m,n)$$

$$\vdots$$

Thus, the discussion given above, as regards the signs of the $Z^{(2i)}$ and the nature of the potential, applies also to the moments $C^{(2i)}$. Furthermore, an asymptotic form for $h(\underline{s})$ in terms of the latter can be written immediately when it is noted that the Fourier inversion of equation (1.3.8) has the same form as equation (1.7.9), i.e.

$$\rho h(\underline{s}) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int \frac{e^{-i\underline{s}\cdot\underline{\omega}}}{1-\rho\tilde{c}(\underline{\omega})} d\underline{\omega}, \quad \underline{s} \neq \underline{0} \tag{1.7.24}$$

The asymptotic expression for $h(\underline{s})$ is obtained by replacing $P(\underline{s};z)$ by $\rho h(\underline{s})$ and the moments $Z^{(2i)}$ by the moments $C^{(2i)}$ in equation (1.7.18).

It can be seen from equation (1.3.5) that

$$1 - C^{(0)} = 1 - \rho \sum_{\underline{s}} c(\underline{s}) = \rho \frac{\partial P}{\partial \rho} > 0, \tag{1.7.25}$$

and, from (1.7.23), that

$$1 - Z^{(0)} = \frac{1-\rho}{P(\underline{0};z)} (1 - C^{(0)}) > 0 \tag{1.7.26}$$

Thus the conditions needed to obtain expression (1.7.19) for T_μ are fulfilled. Since the T_μ decay exponentially with increasing $|\underline{s}|$, the total correlation function $h(\underline{s})$ decays in the same fashion, in accordance with the rigorous result for this type of system [25]. Furthermore, the sum $\sum_{\underline{s}} h(\underline{s})$ in (1.3.4) converges independently of the order of the moments at which the series (1.7.7) is truncated for any practical purpose. The method followed by Throop and Fisk involves truncation of the series (1.7.21), but the convergence of $\sum_{\underline{s}} h(\underline{s})$ depends on both the order of the truncation and the signs of the moments $C^{(2i)}$. This unsatisfactory situation is clearly a consequence of the method employed by these authors (asymptotic inversion) to obtain the form of decay of $h(\underline{s})$. Their asymptotic form for a $2i$-th order truncation, they suggest, has a convergent $\sum_{\underline{s}} h(\underline{s})$ if $(-1)^{i+1} C^{(2i)} > 0$.

We summarize our results for the OZ lattice gas:

(i) When the potential is wholly attractive (except for the essential one-site hard-core), all moments $Z^{(2i)}$ (or $C^{(2i)}$) are positive and $h(\underline{s})$ decays monotonically ($h(\underline{s})>0$ for all $\underline{s} \neq \underline{0}$).

(ii) When the potential is wholly repulsive, all moments $Z^{(2i)}$ (or $C^{(2i)}$) are negative. The nearest neighbour cubic lattice gas has an oscillatory $h(\underline{s})$ with a frequency of oscillation independent of density (and temperature).

(iii) When the potential has both (extended) repulsive and attractive components the weight factors z_j take negative values for the repulsive component and positive values for the attractive tail. The moments $Z^{(2i)}$ (or $C^{(2i)}$) can be either negative or positive depending on the thermodynamic state.

The cubic lattice gas with nearest-neighbour repulsion and next-to-nearest-neighbour attraction has an oscillatory $h(\underline{r})$ with the same frequency of oscillation the correlation of the nearest-neighbour repulsion model has. The appearance of monotonic decay in an extended-core lattice gas will require a longer-ranged attraction as pointed out by Fisher and Widom for the linear lattice gas.

1.8 RANDOM-WALK THEORY AND CONTINUOUS-SPACE SYSTEMS.

It is possible to generalise the random-walk formulation of the lattice gas to include continuous space systems. This can be readily accomplished if we first define the random walk functions for continuous space as suggested by their lattice counterparts.

The step-probability functions $\rho_j(\underline{s})$ for symmetric walks on a periodic lattice can be expressed as

$$\rho_j(\underline{s}) = \frac{1}{l_j} \sum_{\underline{r}_j} \delta_{\underline{s},\underline{r}_j} \quad , \quad \underline{r}_j \in \Gamma_j \quad , \quad j = 0, 1, 2, \ldots , \qquad (1.8.1)$$

where we have included steps of zeroth order or 'zero length', that is, $\Gamma_0 = \{\underline{0}\}$, $\rho_0(\underline{s}) = \delta_{\underline{s},\underline{0}}$ and $l_0 = 1$. The lattice Green's function is

$$P(\underline{s};z) = \frac{1}{(2\pi)^k} \int_{-\pi}^{\pi} \cdots \int \frac{e^{-i\underline{s}\cdot\underline{\theta}} \, d\underline{\theta}}{1 - \sum_{j=0} z_j \lambda_j(\underline{\theta})} \quad , \qquad (1.8.2)$$

where z_0 is the weight factor for steps of zeroth order and $\lambda_0(\underline{\theta}) = 1$. By setting

$$z_j = l_j \rho e_j \quad , \quad e_j = e(\underline{s}) \quad , \quad \underline{s} \in \Gamma_j \quad , \qquad (1.8.3)$$

the total correlation function $h(\underline{s})$ is, in terms of the lattice Green's function, given by

$$\rho h(\underline{s}) = P(\underline{s};z) - \delta_{\underline{s},\underline{0}} \quad . \qquad (1.8.4)$$

We define the step-probability function $p(\underline{s};r)$ for symmetric walks on k-dimensional continuous space, to be the generalised function defined by the properties

$$p(\underline{s};r) = 0 \quad , \quad |\underline{s}| = s \neq r \qquad (1.8.5)$$

and

$$\int_0^\infty \int_\omega p(\underline{s};r) f(\underline{s}) \, ds \, d\omega$$

$$= \frac{1}{2^{k-1}\pi} \int_\omega f(\underline{r}) \frac{d\omega}{r^{k-1}} \, , \qquad (1.8.6)$$

where we have expressed the vector $\underline{s}$ in hyperspherical co-ordinates and where $d\omega$ is the hypersolid angle element. We have assumed the right-hand-side of equation (1.8.6) exists for the sample function $f(\underline{r})$. In one dimension

$$p(s;r) = \tfrac{1}{2}[\delta(s-r) + \delta(s+r)] \, , \qquad (1.8.7)$$

where $\delta(s)$ is the Dirac δ-function, and in three dimensions equation (1.8.6) is

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} p(\underline{s};r) f(\underline{s}) \, ds \, s^2 \sin\psi \, d\psi \, d\varphi$$

$$= \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} f(\underline{r}) \sin\psi \, d\psi \, d\varphi \, . \qquad (1.8.8)$$

$p(\underline{s};r)$ is the normalised probability to step (from the origin) to the point $\underline{s}$ when the length of the step is r.

If we let $P_n(\underline{s};r_1,\ldots,r_n)$ be the probability for the walker to be at point $\underline{s}$ after n steps, the i-th step being of length r_i, we have the recursion formula

$$P_{n+1}(\underline{s};r_1,\ldots,r_{n+1}) = \int_{\text{(all space)}} p(\underline{s}-\underline{s}';r_{n+1}) P_n(\underline{s}';r_1,\ldots,r_n) \, d\underline{s}' \qquad (1.8.9)$$

The probability $P_n(\underline{s};z)$ for the walker to be at $\underline{s}$ after n steps, independently of the length of the steps involved and with respect to the weight function $z(r)$, is defined to be the regular homogeneous functional of degree n

$$P_n(\underline{z};z) = \int_0^\infty \cdots \int_0^\infty P_n(\underline{z};r_1,\ldots,r_n)\, z(r_1)\cdots z(r_n)\, dr_1 \ldots dr_n \,. \quad (1.8.10)$$

The recursion formula for the $P_n(\underline{z};z)$ can be found from equations (1.8.9) and (1.8.10) to be

$$P_{n+1}(\underline{z};z) = \int_{(\text{all space})} \int_0^\infty z(r)\, p(\underline{z}-\underline{z}';r)\, P_n(\underline{z}';z)\, dr\, d\underline{z}' \,. \quad (1.8.11)$$

Finally, we define the probability $P(\underline{z};z)$ for the walker to be at $\underline{z}$, independently of the number and length of the steps involved in the walk, to be the functional power series

$$P(\underline{z};z) = \sum_{n=0}^\infty P_n(\underline{z};z) \,, \quad (1.8.12)$$

and, in accordance with its lattice analogue, we call $P(\underline{z};z)$ the k-dimensional space Green's function.

If we let $\lambda(\underline{\theta};r)$, $W_n(\underline{\theta};r_1,\ldots,r_n)$, $V_n(\underline{\theta};z)$ and $U(\underline{\theta};z)$ be the k-dimensional Fourier transforms of $p(\underline{z};r)$, $P_n(\underline{z};r_1,\ldots,r_n)$, $P_n(\underline{z};z)$ and $P(\underline{z};z)$, respectively, we obtain from equations (1.8.9), (1.8.11) and (1.8.12) the expressions:

$$W_n(\underline{\theta};r_1,\ldots,r_n) = \lambda(\underline{\theta};r_n)\cdots\lambda(\underline{\theta};r_1) \,, \quad (1.8.13)$$

$$V_n(\underline{\theta};z) = \left[\int_0^\infty z(r)\,\lambda(\underline{\theta};r)\,dr\right]^n \,, \quad (1.8.14)$$

$$U(\underline{\theta};z) = \sum_{n=0}^\infty \left[\int_0^\infty z(r)\,\lambda(\underline{\theta};r)\,dr\right]^n \,. \quad (1.8.15)$$

provided $\left|\int_0^\infty z(r)\lambda(\underline{\theta};r)\,dr\right| < 1$, $U(\underline{\theta};z)$ can be written as

$$U(\underline{\theta};z) = \frac{1}{1-\int_0^\infty z(r)\lambda(\underline{\theta};r)\,dr} \,, \quad (1.8.16)$$

so that $P(\underline{z};z)$ satisfies the Green's function equation

$$P(\underline{z};z) - \int_{(\text{all space})} \int_0^\infty z(r)\, p(\underline{z}-\underline{z}';r)\, P(\underline{z}';z)\, dr\, d\underline{z}' = \delta(\underline{z}) \,. \quad (1.8.17)$$

Now, the Ornstein-Zernike relation for a continuous-space homogeneous system is

$$h(\underline{s}) = c(\underline{s}) + \rho \int_{(\text{all space})} c(\underline{s}-\underline{s}')\, h(\underline{s}')\, d\underline{s}' \,, \tag{1.8.18}$$

and Fourier transformation of the above gives

$$\rho \tilde{h}(\underline{\theta}) = \frac{1}{1-\rho \tilde{c}(\underline{\theta})} - 1 \,, \tag{1.8.19}$$

where, for spherically symmetric correlation functions,

$$\begin{aligned} \rho \tilde{c}(\underline{\theta}) &= \int_0^\infty \int_\omega \rho c(r)\, e^{i \underline{r}\cdot\underline{\theta}}\, dr\, d\omega \\ &= \int_0^\infty (2r)^{k-1} \pi \rho c(r) \left\{ \frac{1}{2^{k-1}\pi} \int_\omega e^{i \underline{r}\cdot\underline{\theta}} \frac{d\omega}{r^{k-1}} \right\} dr \\ &= \int_0^\infty (2r)^{k-1} \pi \rho c(r)\, \lambda(\underline{\theta}; r)\, dr. \end{aligned} \tag{1.8.20}$$

If we define the weight function $z(r)$ as

$$z(r) = (2r)^{k-1} \pi \rho c(r) \tag{1.8.21}$$

we obtain, from equations (1.8.16), (1.8.19) and (1.8.20),

$$\rho h(\underline{s}) = P(\underline{s}; z) - \delta(\underline{s}) \tag{1.8.22}$$

and, if by $\mathcal{F}$ and $\mathcal{F}^{-1}$ we denote Fourier and inverse Fourier transformation, respectively, equations (1.8.15), (1.8.20) and (1.8.22) give

$$\rho h(\underline{s}) = \sum_{n=1}^{\infty} \mathcal{F}^{-1} \left\{ \mathcal{F} [\rho c(\underline{s})] \right\}^n . \tag{1.8.23}$$

This equation, a Markovian chain expression, can be also obtained from the OZ relation when solved for $h(\underline{s})$ by interation.

A similar expression for the pair distribution function,

but restricted to one-dimensional systems with nearest-neighbour interactions, has been obtained by Salsburg, Zwanzig and Kirkwood[14], and was later interpreted as a random walk problem by Harris, Sells and Guth[26]. In their analysis the weight function $z(r)$ is the distribution function for adjacent particles. i.e.:

$$z(r) = \frac{e^{-cr-\beta\varphi(r)}}{\int_0^\infty e^{-cs-\beta\varphi(s)}\,ds} \qquad (1.8.24)$$

where

$$c = -\beta\int_0^\infty z(s)\,\varphi'(s)\,ds ,$$

so that steps of length not exceeding the range of the hard core are excluded. In our case, steps of this length are most favoured, for $z(r)$ is the direct correlation function.

The method employed by Salsburg et al does not seem capable of extension to two and three dimensions. The fact that in one dimension nearest-neighbour interactions (with the essential hard core) enforce an ordering of the particles is crucial in the derivation[14,26]. On the other hand, when we identify $z(r)$ with the direct correlation function we are no longer restricted by dimensionality or by the range of the potential. However equation (1.8.24) is exact whereas in our case we have to employ one of the several existing expressions for $c(s)$ in terms of $\varphi(s)$ and the particle distribution functions (such as the PY approximation).

There is another possibility, and that is to consider the weight function being determined by some maximum principle. A generalised Ornstein-Zernike relation proposed by Green[27], and based on a maximum principle in which the variations are performed on the system

of particle distribution functions, gives us an answer, but not unexpectedly opens new and more complex questions. The quantity to be maximised is the functional

$$\log \Xi = S(\psi) + \sum_{\nu=1}^{\infty} \frac{1}{n!} \int \psi([n]) f([n]) d[n] \qquad (1.8.25)$$

where $f([n])$ is the distribution function for n particles, $\psi([n])$ is given by

$$\psi([n]) = \sum_{[\nu] \subseteq [n]} (-1)^{n-\nu} \log f([\nu]) \qquad (1.8.26)$$

and $S(\psi)$ is the expression for the entropy as a functional of the distribution functions. The maximum value attained by $\log \Xi$ is the logarithm of the grand partition function[27]. The generalised OZ relation is expressed in terms of the elements of both the direct correlation matrix $T([m],[n])$ and the total correlation matrix $G([m],[n])$, as follows[27]:

$$\sum_{\mu=1}^{\infty} \frac{1}{\mu!} \int T([n],[\mu]) G([\mu],[n']) d[\mu] = \delta([n],[n']) \qquad (1.8.27)$$

where the elements $T([m],[n])$ and $G([m],[n])$ correlate a set of m particles to another set of n particles, and the δ-type term $\delta([n],[m])$ contributes only when the set of particles $[n]$ coincides with the set $[m]$. The total correlation matrix element $G([m],[n])$ is given by a finite number of terms involving only the distribution functions in the set $\{f([n']) \mid n' \leq n, m\}$, whereas the direct correlation matrix element $T([m],[n])$ is given by a finite number of terms involving the particle potential and the distribution functions in the set $\{f([n']) \mid n' \leq n, m\}$. When equation (1.8.27) is specialised to the case $n = m = 1$ and all other elements $T(1,[n])$ are set equal to zero one obtains the PY

approximation[27], since $T(1,1')$ and $G(1,1')$ are given by

$$T(1,1') = T(\underline{1}) = \rho\delta(\underline{1}) - \rho^2(1-e^{\beta\varphi(\underline{1})})(h(\underline{1})+1) \tag{1.8.28}$$

and

$$G(1,1') = G(\underline{1}) = \rho^{-1}\delta(\underline{1}) + h(\underline{1}). \tag{1.8.29}$$

If we now define $T(1,1')$ in terms of the weight function as

$$T(\underline{1}) = \rho\delta(\underline{1}) - \rho\int_0^\infty z(r)\,p(\underline{1};r)\,dr, \tag{1.8.30}$$

and write

$$G(\underline{1}) = \rho^{-1}\,P(\underline{1};z), \tag{1.8.31}$$

in accordance with equations (1.8.22) and (1.8.29), then, the Green's function equation (1.8.17) is equivalent to equation (1.8.27) when $n=m=1$ and all other $T(1,[n])=0$. Thus, when three-particle and higher-order correlations are neglected, a maximum principle for statistical mechanics determines the weight function in terms of the particle potential and this leads to the PY approximation.

Any improvement along these lines, to produce a random-process description of the next terms in the generalised OZ relation, will require a generalization of the concept we have employed here for a random walk. It must be stressed that the interpretation of the first term in equation (1.8.27) in terms of (independent) walks connecting particles 1 and 1' is possible because two-particle correlations can only relate pairs of particles. When higher-order correlations are taken into account we would have to think of the problem as a branching process. In the analysis of the

general term $T([n],[\mu])G([\mu],[m])$ one might have to replace the concept of walk by that of a 'directed net' originating at the set of particles $[n]$, terminating at the set of particles $[m]$ and with a branching rule given by the number of particles in $[\mu]$ The nature of this problem is reminiscent of that for the percolation[28] and other related branching processes[29] and one might hope that progress towards the precise formulation and the solution of the combinatorial problems set up by the higher-order terms of equation (1.8.27) can be achieved when a link is established with these, better known, random processes. The interpretation of the elements $T(1,1')$ and $G(1,1')$ is likely to remain as given above, and the fact that the length of the steps in the walks would then be restricted to the range of the potential function is physically more appealing.

Of course, the foregoing comments also apply to lattice systems.

CHAPTER TWO

APPLICATION OF THE RANDOM-WALK APPROACH TO SPECIFIC LATTICE-GAS MODELS

21. INTRODUCTION

In this chapter we apply the formalism developed previously to some particular one - and two-dimensional lattice-gas models and give a brief account of the properties exhibited by these systems. They are all treated under the PY approximation and the method followed consists essentially in the resolution of the system of equations for the weight factors of either the homogeneous or the inhomogeneous gas (see equations (1.4.3), (1.4.4), (1.5.26) amd (1.5.27)). We show, by graphs, the dependence of the weight factors and the correlation functions on the density of these systems for both infinite and finite interactions (and on the temperature for the latter).

We chose to consider first the one-dimensional lattice gas with nearest-neighbour interactions. The simple form that all expressions take for this model leads to closed-form results for infinite repulsion, and since in this case the PY approximation is exact they are also rigorous results. In our next examples we had to resort to numerical resolution of the above-mentioned system of equations; for this reason and because of the similarity of the expressions for all models considered, we merely evaluate the lattice Green's function and discuss the final results. The effect of extending the range of the interaction is studied for the linear lattice gas with nearest - and next-to-nearest neighbour interactions. We then turn our attention to two-dimensional

systems and discuss the phase transition of the square lattice gas with nearest-neighbour exclusion; we also describe some aspects of the duplication of this transition when the interaction is turned into a soft repulsion. Finally, we show how the general approach can be modified to include lattice gases where the geometrical arrangement of sites prevents all sites in the lattice from being equivalent.

Lattice gas models with even-longer-ranged potentials can obviously be studied by this method. However, the increased number of equations (particularly for the ordered phases because more sublattices have to be introduced) and the well known inaccuracy of the PY approximation at high densities discouraged us from doing so. However, we studied the square lattice gas with nearest and next-to-nearest-neighbour exclusion within the two-sublattice framework. We comment briefly on our results for this model.

2.2 ONE-DIMENSIONAL LATTICE GASES.

A. Linear Lattice Gas with Nearest-Neighbour Interactions. (L1 model).

The weight function for this model is

$$z(s) = \frac{z_1}{2}, \quad s = \pm 1$$

$$z(s) = 0 \quad \text{otherwise,} \tag{2.2.1}$$

and the random-walk generating functions are given by

$$P(s; z_1) = \frac{1}{2\pi} \int_0^{\pi} \frac{\cos s\theta}{1 - z_1 \cos\theta} \, d\theta$$

$$= \frac{\left[1 - (1 - z_1^2)^{\frac{1}{2}}\right]^{|s|}}{(1 - z_1^2)^{\frac{1}{2}} z_1^{|s|}} \tag{2.2.2}$$

and

$$F(s; z_1) = \frac{P(s; z_1) - \delta_{s,0}}{P(0; z_1)}$$

$$= \frac{\left[1 - (1 - z_1^2)^{\frac{1}{2}}\right]^{|s|}}{z_1^{|s|}} - (1 - z_1^2)^{\frac{1}{2}} \delta_{s,0} . \tag{2.2.3}$$

The correlation functions for the inhomogeneous gas become

$$c_0^{(1)} = \rho_1^{-1} \left\{ 1 - \left[(1 - \rho_1)(1 - z_1^2)^{\frac{1}{2}} \right]^{-1} \right\},$$

$$c_0^{(2)} = \rho_2^{-1} \left\{ 1 - \left[(1 - \rho_2)(1 - z_1^2)^{\frac{1}{2}} \right]^{-1} \right\},$$

$$c_1^{(3)} = \frac{z_1}{2} \left\{ \rho_1 \rho_2 (1 - \rho_1)(1 - \rho_2)(1 - z_1^2) \right\}^{-\frac{1}{2}} \tag{2.2.4}$$

and

$$h^{(ij)}(s) = \left[\rho_i^{-1} \rho_j^{-1} (1 - \rho_i)(1 - \rho_j) \right]^{\frac{1}{2}} \times$$

$$\times \left\{ 1 - (1 - z_1^2)^{\frac{1}{2}} \right\}^{|s|} z_1^{-|s|}, \quad s \neq 0; \; i, j = 1, 2. \tag{2.2.5}$$

The PY condition

$$c_1^{(3)} = \left(h^{(12)}(\pm 1) + 1 \right)(1 - e^{\beta\omega}) , \tag{2.2.6}$$

where ω is the interaction between nearest-neighbour sites, determines the weight factor z_1, in terms of the sublattice densities ρ_1 and ρ_2, i.e. z_1 is a root of the equation

$$\left[\rho_1^{-1}\rho_2^{-1}(1-\rho_1)(1-\rho_2)\right]^{\frac{1}{2}}\left\{1-(1-z_1^2)^{\frac{1}{2}}\right\}z_1^{-1}$$
$$-\frac{z_1}{2}\left\{\left[\rho_1\rho_2(1-\rho_1)(1-\rho_2)(1-z_1^2)\right]^{\frac{1}{2}}(1-e^{\beta\omega})\right\}^{-1}+1=0\,. \qquad (2.2.7)$$

Now, from equations (1.6.8) and (1.6.9) we have, for the partially-coupled correlation function, the expressions

$$h^{(11)}(0;\xi)=\frac{1}{\rho_1}\left\{\frac{\rho_1 c_0^{(1)}(\xi)c_1^{(3)}+(1-\rho_1 c_0^{(1)})c_1^{(3)}(\xi)}{c_1^{(3)}(1-\rho_1 c_0^{(1)})(1-z_1^2)^{\frac{1}{2}}}-\frac{c_1^{(3)}(\xi)}{c_1^{(3)}}\right\} \qquad (2.2.8)$$

and

$$h^{(12)}(\pm1;\xi)=\frac{c_1^{(3)}(\xi)(1-\rho_1 c_0^{(1)})+\rho_1 c_1^{(3)}c_0^{(1)}(\xi)}{c_1^{(3)}\left[\rho_1\rho_2(1-\rho_1 c_0^{(1)})(1-\rho_2 c_0^{(2)})\right]^{\frac{1}{2}}}\,\frac{1-(1-z_1^2)^{\frac{1}{2}}}{z_1(1-z_1^2)^{\frac{1}{2}}}\,. \qquad (2.2.9)$$

These equations can be solved for $h^{(12)}(\pm1;\xi)$ when the conditions

$$h^{(11)}(0;\xi)=-1$$
$$c_1^{(3)}(\xi)=(h^{(12)}(\pm1;\xi)+1)(1-e^{\beta\xi\omega}) \qquad (2.2.10)$$

and equations (2.2.4) are taken into account. The result is

$$g^{(12)}(\pm1;\xi)=h^{(12)}(\pm1;\xi)=\frac{c_1^{(3)}}{(1-e^{\beta\xi\omega})+c_1^{(3)}(1-\rho_1)}\,. \qquad (2.2.11)$$

When the above is substituted into (1.6.1) and the integral with respect to ξ is performed, we obtain for the activity γ_1 of the sublattice gas I the expression

$$\gamma_1=\frac{\rho_1}{1-\rho_1}\exp\left\{\frac{z\rho_2 c_1^{(3)}}{c_1^{(3)}(1-\rho_1)+1}\left[\beta\omega-\log\left|c_1^{(3)}(1-\rho_1)+1-e^{\beta\omega}\right|\right.\right.$$
$$\left.\left.+\log\left|c_1^{(3)}\right|(1-\rho_1)\right]\right\}. \qquad (2.2.12)$$

Similarly, the activity γ_2 of the sublattice gas II is given by

$$\gamma_2 = \frac{\rho_2}{1-\rho_2} \exp\left\{ \frac{2\rho_1 c_1^{(3)}}{c_1^{(3)}(1-\rho_2)+1} \left[\beta\omega - \log\left| c_1^{(3)}(1-\rho_2) + 1 - e^{\beta\omega} \right| + \log\left| c_1^{(3)} \right| (1-\rho_2) \right] \right\} . \qquad (2.2.13)$$

The problem of determining the density solutions, and the density dependence of the correlation functions, consists now in the resolution of the set of equations (2.2.4), (2.2.7), (2.2.12) and (2.2.13) with the condition $\gamma_1 = \gamma_2$. Before presenting the results for a finite interaction ω, we look at the case $\omega \to \infty$ for which closed-form expressions can be obtained.

When $\omega \to \infty$ equations (2.2.7), (2.2.12) and (2.2.13) take the form

$$\left[\rho_1^{-1}\rho_2^{-1}(1-\rho_1)(1-\rho_2)\right]^{\frac{1}{2}} \left\{ 1 - (1-z_1^2)^{\frac{1}{2}} \right\} z_1^{-1} + 1 = 0 , \qquad (2.2.14)$$

$$\gamma_1 = \frac{\rho_1}{1-\rho_1} \exp\left\{ \frac{2\rho_2 c_1^{(3)}}{c_1^{(3)}(1-\rho_1)+1} \log\left[(1-\rho_1) \left| c_1^{(3)} \right| \right] \right\} , \qquad (2.2.15)$$

$$\gamma_2 = \frac{\rho_2}{1-\rho_2} \exp\left\{ \frac{2\rho_1 c_1^{(3)}}{c_1^{(3)}(1-\rho_2)+1} \log\left[(1-\rho_2) \left| c_1^{(3)} \right| \right] \right\} . \qquad (2.2.16)$$

Now, if we set

$$z_1 = -\sin u \quad , \quad 0 \le u \le \frac{\pi}{2} \qquad (2.2.17)$$

($|z_1| \le 1$, see equation (1.2.14)), equation (2.2.14) can be written as

$$\left[\rho_1\rho_2(1-\rho_1)^{-1}(1-\rho_2)^{-1}\right]^{\frac{1}{2}} = \tan\frac{u}{2} \qquad (2.2.18)$$

or as

$$P(0;z_1) = (1-z_1^2)^{-\frac{1}{2}} = 1 + \left[\rho_1\rho_2(1-\rho_1)^{-1}(1-\rho_2)^{-1}\right]^{\frac{1}{2}} \tan u . \qquad (2.2.19)$$

Elimination of $\mathcal{U}$ in these last two equations leads us to

$$z_1 = -\frac{2[\rho_1\rho_2(1-\rho_1)(1-\rho_2)]^{\frac{1}{2}}}{(1-\rho_1)(1-\rho_2)+\rho_1\rho_2}, \tag{2.2.20}$$

$$P(0;z_1) = \frac{(1-\rho_1)(1-\rho_2)+\rho_1\rho_2}{1-\rho_1-\rho_2}, \tag{2.2.21}$$

$$c_1^{(3)} = -\frac{1}{1-\rho_1-\rho_2}, \tag{2.2.22}$$

and by equating the right-hand-sides of equations (2.2.15) and (2.2.16), with $c_1^{(3)}$ given by equation (2.2.22), we obtain the density solutions

$$\rho_1 = \rho_2$$
$$\rho_1 = 1-\rho_2 \tag{2.2.23}$$

For the fluid-type solution $\rho = \rho_1 = \rho_2$, $0 \le \rho \le \frac{1}{2}$, we have

$$z_1 = -\frac{2\rho(1-\rho)}{(1-\rho)^2+\rho^2} \tag{2.2.24}$$

$$P(0;z_1) = \frac{(1-\rho)^2+\rho^2}{1-2\rho} \tag{2.2.25}$$

$$c_0 = -\frac{1}{(1-2\rho)(1-\rho)} \tag{2.2.26}$$

$$c_1 = -\frac{1}{1-2\rho} \tag{2.2.27}$$

$$h(s) = (-1)^s\left(\frac{\rho}{1-\rho}\right)^{|s|-1}$$
$$= (-1)^s(\rho^{-1}-1)\,e^{-k|s|},\quad k = \ln(\rho^{-1}-1),\quad s \neq 0,\pm 1. \tag{2.2.28}$$

$$\gamma = \frac{\rho(1-\rho)}{(1-2\rho)^2} \tag{2.2.29}$$

$$\beta\frac{\partial P}{\partial \rho} = \frac{\rho}{\gamma}\frac{\partial \gamma}{\partial \rho} = -c_0 = \frac{1}{(1-\rho)(1-2\rho)} \tag{2.2.30}$$

$$\beta P = \log \frac{1-\rho}{1-2\rho} \quad . \tag{2.2.31}$$

The OZ assumption is satisfied by the linear hard-core lattice gas[30]. Equations (2.2.24) to (2.2.31) are the exact expressions for this model.

The second density solution, $\rho_1 = 1 - \rho_2$ occurs at close packing ($\rho = (\rho_1+\rho_2)/2$, $z_1 = -1$ and infinite activity). It can be regarded as an atrophied solid phase representing all configurations at close packing. The system shows no phase transition, a feature common to all one-dimensional systems with finite range interactions[31].

It is also possible to obtain exact expressions for the three-particle total and direct correlation functions for this model. These functions are defined by[12]:

$$h_3(r,s) = g_3(r,s) - g(r) - g(s) - g(r-s) + 2 \tag{2.2.32}$$

and

$$\begin{aligned}
&h_3(r,s) - h(r)h(s-r) - h(s)h(r-s) - h(r)h(s) - c_3(r,s) \\
&= \rho \sum_t h(t)h(r-t)h(s-t) + \rho \sum_{r'} c_3(r',s)h(r-r') \\
&+ \rho \sum_{s'} c_3(r,s')h(s-s') + \rho \sum_{r'} c_3(r',s-r+r')h(r-r') \\
&+ \rho^2 \sum_{r'} \sum_{s'} c_3(r',s')h(r-r')h((s-r)-(s'-r')) \\
&+ \rho^2 \sum_{r'} \sum_{s'} c_3(r',s')h(s-s')h((s-r)-(s'-r')) \\
&+ \rho^2 \sum_{r'} \sum_{s'} c_3(r',s')h(r-r')h(s-s') \\
&+ \rho^3 \sum_{r'} \sum_{s'} \sum_t c_3(r',s')h(t)h((s-s')-t)h((r-r')-t)
\end{aligned} \tag{2.2.33}$$

where $h_3(r,s)$ and $c_3(r,s)$ are the three-particle total and direct correlation functions, respectively, and where $g_3(r,s)$ is the three-particle distribution function. The three-and two-particle direct correlation functions are related by the simple expression[12,13]

$$\frac{\partial}{\partial \rho} c(r) = \sum_s c_3(r,s) . \qquad (2.2.34)$$

For a one-dimensional system interacting only by means of a hard core, the function $c_3(r,s)$ vanishes when the distance between any two particles exceeds the range of the interaction[13]. Then, for nearest-neighbour exclusion $c_3(r,s)$ takes only two values

$$\begin{aligned} c_{00} &= c_3(0,0) , \\ c_{10} &= c_3(\pm 1,0) = c_3(0,\pm 1) = c_3(1,1) = c_3(-1,-1) , \end{aligned} \qquad (2.2.35)$$

and from equation (2.2.34) we obtain

$$\begin{aligned} c_{00} &= \frac{\partial}{\partial \rho}(c_0 - c_1) , \\ c_{10} &= \frac{1}{2}\frac{\partial c_1}{\partial \rho} . \end{aligned} \qquad (2.2.36)$$

Now, if we replace $\rho h(s)$ by $P(s;z_1)(1-\rho c_0)^{-1} - \delta_{s,0}$ in equation (2.2.33) we obtain the simpler expression

$$\rho^2 h_3(r,s) = \frac{\rho^2}{(1-\rho c_0)^3} \sum_{r'} \sum_{s'} \sum_t c_3(r',s') P(t;z_1) \times$$

$$\times P((s-s')-t;z_1) P((r-r')-t;z_1) + \sum_t \frac{P(t;z_1) P(r-t;z_1) P(s-t;z_1)}{(1-\rho c_0)^3}$$

$$- \frac{P(r-s;z_1)}{1-\rho c_0}(\delta_{s,0}+\delta_{r,0}) - \frac{P(s,z)}{1-\rho c_0}\delta_{s,r} + \delta_{s,0}\delta_{r,0} . \qquad (2.2.37)$$

The results for the PY L1 model are summarized in figures 1 to 8. It can be observed from figure 1 that for a finite interaction ω (and a fixed temperature) there is an intermediate density at which walks involving a large number of steps

are given a maximum of 'participation' ($|z_1|$ is a maximum). Away from this density, walks involving fewer number of steps become more important. When the interaction is infinitely repulsive, the maximum of $|z_1|$ occurs at close packing. The dependence of the direct correlation function on the density and on the weight factor z_1, for various temperatures, are shown in figures 2 to 6 for both repulsive and attractive interactions. The total correlation function is shown as a function of the density for various distances in figures 7 and 8.

B. Linear Lattice Gas With Nearest - and Next-to-Nearest-Neighbour Interactions (L12 model)

The lattice Green's function for the L12 model is given by

$$P(s;z_1,z_2) = \frac{1}{\pi}\int_0^{\pi} \frac{\cos s\theta \, d\theta}{1 - z_1\cos\theta - z_2\cos 2\theta} \,. \tag{2.2.38}$$

In particular

$$P(0;z_1,z_2) = \frac{1}{(1+z_1-z_2)(\alpha-\beta)}\left\{\frac{1+\alpha}{|\alpha|^{\frac{1}{2}}} - \frac{1+\beta}{|\beta|^{\frac{1}{2}}}\right\} \tag{2.2.39}$$

and

$$P(1;z_1,z_2) = \frac{1}{(1+z_1-z_2)(\alpha-\beta)}\left\{\frac{1-\alpha}{|\alpha|^{\frac{1}{2}}} - \frac{1-\beta}{|\beta|^{\frac{1}{2}}}\right\} \tag{2.2.40}$$

where

$$\alpha = \frac{-(1+3z_2)+D^{\frac{1}{2}}}{1+z_1-z_2}$$

$$\beta = \frac{-(1+3z_2)-D^{\frac{1}{2}}}{1+z_1-z_2}$$

$$D = (1+3z_2)^2 - (1-z_1-z_2)(1+z_1-z_2) > 0 \,,$$

and

$$P(0;z_1,z_2) = \frac{i}{(1+z_1-z_2)(\alpha-\beta)}\left\{\frac{1+\alpha}{\alpha^{\frac{1}{2}}} - \frac{1+\beta}{\beta^{\frac{1}{2}}}\right\} \tag{2.2.41}$$

and

$$P(1;z_1,z_2) = \frac{i}{(1+z_1-z_2)(\alpha-\beta)}\left\{\frac{1-\alpha}{\alpha^{\frac{1}{2}}} - \frac{1-\beta}{\beta^{\frac{1}{2}}}\right\} \qquad (2.2.42)$$

where

$$\alpha = \frac{-(1+3z_2)+i(-D)^{\frac{1}{2}}}{1+z_1-z_2}$$

$$\beta = \frac{-(1+3z_2)-i(-D)^{\frac{1}{2}}}{1+z_1-z_2}, \quad D<0.$$

The value of $P(s;z_1,z_2)$ for arbitrary s can be found from the values of $P(0;z_1,z_2)$ and $P(1;z_1,z_2)$ by means of the recursion formula (the lattice Green's equation for this model)

$$P(s;z_1,z_2) - \frac{z_1}{2}P(s-1;z_1,z_2) - \frac{z_1}{2}P(s+1;z_1,z_2)$$
$$- \frac{z_2}{2}P(s-2;z_1,z_2) - \frac{z_2}{2}P(s+2;z_1,z_2) = \delta_{s,0}. \qquad (2.2.43)$$

The results for the PY L12 model are shown in figures 9 to 14. We have considered first-neighbour exclusion followed by either second-neighbour exclusion or finite interaction. Figure 9 shows the weight factor solutions in the $z_1 \times z_2$-plane; z_2 is positive for an attractive interaction and negative for a repulsive one. The dependence of z_1 and z_2 on ρ is shown in figures 10 and 11 where it can be observed that even for second-neighbour exclusion

steps to first neighbours are favoured at all densities. In figures 12 and 13 we show the direct correlation function as a function of density. Figure 14 shows the total correlation function at various distances as a function of density; the change in sign of $h(4)$ and of $h(6)$ suggests that the frequency of oscillation of the asymptotic $h(s)$ is density dependent. We recall that (see section 1.7), in the case of first-neighbour exclusion and second-neighbour

attraction, $h(s)$ $(= (-1)^s |h(s)|)$ oscillates in the same way as for first-neighbour exclusion only; monotonic decay is ruled out for such a short-ranged attraction.

2.3 TWO-DIMENSIONAL LATTICE GASES.

A. Square Lattice Gas with Nearest-Neighbour Interactions (SQ1 model)

This model is specified by the weight function

$$Z(\underline{s}) = \frac{z_1}{4} \quad , \quad \underline{s} = (\pm 1, 0), (0, \pm 1)$$

$$Z(\underline{s}) = 0 \qquad \text{otherwise,} \tag{2.3.1}$$

for which the lattice Green's function becomes

$$P(\underline{s}; z_1) = \frac{1}{\pi^2} \int_0^{\pi}\int_0^{\pi} \frac{\cos s_1\theta_1 \cos s_2\theta_2 \, d\theta_1 d\theta_2}{1 - \frac{z_1}{2}(\cos\theta_1 + \cos\theta_2)} \tag{2.3.2}$$

In particular, for $\underline{s}=(0,0)$ and $\underline{s}=(1,1)$ we obtain

$$P(0,0; z_1) = \frac{2}{\pi} K(|z_1|) \tag{2.3.3}$$

and

$$P(1,1; z_1) = \frac{2}{\pi}\left[\left(\frac{2}{z_1^2} - 1\right) K(|z_1|) - \frac{2}{z_1^2} E(|z_1|)\right] \tag{2.3.4}$$

where K and E are the complete elliptic integrals of the first and second kind, respectively. The value of $P(\underline{s}; z_1)$ for arbitrary $\underline{s}$ can be found from the above by interated use of the lattice Green's equation

$$P(s_1, s_2; z_1) - \frac{z_1}{4}\Big[P(s_1+1, s_2; z_1) + P(s_1-1; s_2; z_2) + P(s_1, s_2+1; z_1) + P(s_1, s_2-1; z_1)\Big] = \delta_{\underline{s},\underline{0}} \tag{2.3.5}$$

together with the symmetry properties of $P(\underline{s}; z_1)$. i.e.:

$$P(s_1, s_2; z_1) = P(s_2, s_1; z_1)$$

and

$$P(s_1, s_2; z_1) = P(-s_1, s_2; z_1) . \tag{2.3.6}$$

The expressions for the correlation functions and activities of the inhomogeneous lattice gas are similar to those given for

the L1 model, and the density solutions for the PY approximation are determined by a set of equations analogous to that for the L1 model. We omit them to avoid duplication.

Our results for the PY SQ1 model are shown in figures 15 to 21. We have considered the cases of infinite and soft repulsions only.

The sublattice densities solutions for the case of first-neighbour exclusion are shown in figure 15a. The fluid-type solution extends up to the close-packing density $\rho = 0.5$ and a solid-type solution intersects the former at a transition density $\rho = 0.275$ The PY system exhibits a second-order Ehrenfest phase transition as indicated by a finite discontinuity in the quantity $\frac{\partial \gamma}{\partial \rho}$, with $\frac{\partial \gamma}{\partial \rho} \neq 0$ at the transition density (see figure 16). The Padé approximant and transfer matrix results for this model, which are free from any underlying approximation such as PY, differ from ours both in the type of transition and the value of the transition density. The Padé approximant method[19] predicts a continuous (second order) transition with $\frac{\partial \gamma}{\partial \rho} \neq 0$ at a transition density $\rho = 0.370 \pm 4$ whereas the transfer matrix method[32] predicts again a continuous transition but of the λ-type, that is, with $\frac{\partial \gamma}{\partial \rho} = 0$ at the transition density $\rho = 0.369$. This discrepancy between PY results and the more exact Padé and matrix results is found also for the cubic lattice gas with first neighbour exclusion[2].

In figure 17 we can see the weight factor $\mathbb{Z}_1$, as a function of density for both the fluid and the solid phases. The value of $|\mathbb{Z}_1|$ for the fluid phase increases as the transition density is approached and the transition occurs at a relatively large value for $|\mathbb{Z}_1|$ ($|\mathbb{Z}_1|_T$), an indication that walks involving a large number of steps make a substantial

contribution to the value the Green's function takes at this density. The value of $|z_1|$ for the solid phase decreases as close packing is approached. Walks with few steps dominate in $P(\underline{s};z_1)$ as the interactions become more localized and an ordered arrangement of particles is adopted by the system. The meta-stable fluid (the fluid-type solution at densities higher than the transition density) occurs for values of $|z_1|$ greater than $|z_1|_T$, and at the 'fluid' close-packing $|z_1| = 1$.

The isothermal compressibility for the fluid phase is given by

$$\beta^{-1}K = \rho^{-1}\left[1-\rho\sum_{\underline{s}} c(\underline{s})\right]^{-1} = -\frac{1}{\rho c_0} \tag{2.3.7}$$

and since

$$\rho c_0 = 1 - \frac{P(\underline{o};z_1)}{1-\rho} \tag{2.3.8}$$

and

$$F(\underline{o};z_1) = 1 - \left[P(\underline{o};z_1)\right]^{-1} \tag{2.3.9}$$

we obtain

$$\beta^{-1}K = \frac{(1-\rho)\left[1-F(\underline{o};z_1)\right]}{\rho+(1-\rho)F(\underline{o};z_1)} . \tag{2.3.10}$$

Similarly, for the solid phase we have (see equation (1.5.29))

$$\beta^{-1}K = -\frac{2}{\rho_1 c_0^{(1)} + \rho_2 c_0^{(2)}}$$

$$= 2\left\{\frac{\rho_1+(1-\rho_1)F(\underline{o};z_1)}{(1-\rho_1)\left[1-F(\underline{o};z_1)\right]} + \frac{\rho_2+(1-\rho_2)F(\underline{o};z_1)}{(1-\rho_2)\left[1-F(\underline{o};z_1)\right]}\right\}^{-1} . \tag{2.3.11}$$

The behaviour of the compressibility may be interpreted in terms of the number of holes returning to their original sites, with $1-\rho$ as the density of holes and $F(\underline{o};z_1)$ and

$[1-F(Q;z_1)]$ as, respectively, the return and escape probabilities at density $\rho(z_1)$. (In fact equation (2.3.10) is valid for any lattice gas interacting only via a hard core). At close packing we have $z_1=0$ for the solid and $|z_1|=1$ for the metastable fluid and since $F(Q;0)=0$ and the probability of the walker to return to the origin is unity in two dimensions[6], equations (2.3.10) and (2.3.11) predict $K=0$ at this density.

In figures 18 and 19 we show the correlation functions as functions of density, for both fluid and solid phases.

As we mentioned in section 1.4, the effect of the OZ assumption is to restrict the length of the steps in the walks to be within the range of the potential function. In order to estimate the extent to which longer steps contribute to the 'exact' Green's function, we have evaluated the weight factors (as functions of density), for walks involving steps to first-and to second-neighbouring sites, that reproduce the Padé approximant data for the compressibility of the fluid phase[33]. That is we have solved

$$\frac{\beta(1-\rho)}{\rho K_{Padé}} = P(0,0;z_1,z_2)(1-z_1-z_2) \qquad (2.3.12)$$

together with the boundary condition

$$-1 = \frac{1-\rho}{\rho}\,\frac{P(1,0;z_1,z_2)}{P(0,0;z_1,z_2)} \qquad (2.3.13)$$

where

$$P(s_1,s_2;z_1,z_2) = \frac{1}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\frac{\cos s_1\theta_1 \cos s_2\theta_2\, d\theta_1 d\theta_2}{1-\frac{z_1}{z}(\cos\theta_1+\cos\theta_2)-z_2\cos\theta_1\cos\theta_2} \qquad (2.3.14)$$

The results are summarized in figures 20 and 21. A sample calculation, not included here, suggests that consideration of third-order steps would reduce the value of z_2 as z_3

becomes important, while $\mathcal{Z}_1$ is basically unaltered.

As long as we identify the weight function with the direct correlation function, the fact that the hard core SQl model exhibits a continuous transition forces us to consider steps of order higher than one, and these become increasingly important as the transition density is approached (from the fluid phase), and would eventually dominate over those to first-neighbour sites if the compressibility is to become infinite at the transition point. If, instead,we identify the weight function with the lowest direct correlation matrix element (see section 1.8), the effect of first-neighbour-site steps on the compressibility would have to be balanced by that of the three- (and more) particle correlation matrix elements.

As regards the SQlmodel with soft repulsion (treated under the PY approximation) we record in figures 15b and 17 some features of its most interesting property: The duplication of the second order (Ehrenfest) phase transition. Hemmer and Stell[34,35] discovered that a second transition can be induced in a system already exhibiting one transition by the softening of the hard-core repulsion. The general argument given by these authors to explain the duplication of a transition in lattice systems is based on the particle-hole symmetry that exists between occupied and unoccupied sites in the lattice. And a consequence of this symmetry is that for a lattice gas with nearest-neighbour finite interactions the thermodynamic states occur in conjugate pairs[36], that is, given a state at density ρ and temperature T its conjugate pair is located at density $\rho' = 1-\rho$ and at the same temperature T. For infinite repulsion conjugate states do not appear but by softening this repulsion it is

possible to preserve the original transition and to unfold the particle-hole symmetry to yield the second transition.

In figure 15b we show the density solutions for the interaction $\beta\omega = 2.5$. There is a fluid-type solution extending from $\rho = 0$ to $\rho = 1$ and two solid-type solutions intersecting the fluid line. The first transition appears at a density higher than that for infinite repulsion and the 'malformation' of the solid solutions (particularly the second solid branch) is probably a consequence of the PY approximation. In figure 17 we show the weight factor solution, and again, the lack of symmetry about the density $\rho = \frac{1}{2}$ is probably due to the same reasons. As the temperature is increased the two transition densities appear at values closer to each other and to $\rho = \frac{1}{2}$. The same happens to the values of the weight factor at the transition points, they both appear nearer $z_1 = -1$. Eventually the fluid solution fails to attain the value $z_1 = -1$ and the solid solutions disappear; thus the system can exist only in a fluid phase at higher temperatures (see figure 17 for $\beta\omega = 1$).

We have also studied the square lattice gas with nearest- and next-to-nearest-neighbour exclusion (hard core SQ12 model). The lattice Green's function for the homogeneous gas is that in equation (2.3.14). The results for the fluid phase of this model do not differ qualitatively from those for the hard core L12 model and for this reason we do not include them. The two-sublattice gas does not show a solid-type solution, and we believe that even the inclusion of more sublattices would not enable us to settle the question of whether this model exhibits a phase transition[37,38,39].

B. HONEYCOMB LATTICE GAS WITH NEAREST-NEIGHBOUR INTERACTIONS. (H1 MODEL)

The derivation of our basic random-walk equations has to be extended somewhat to cover lattices that differ from the k-D simple cubic lattices in that not all sites in the lattice are equivalent. For this purpose the special case of interest here will be the honeycomb or hexagonal lattice.

Consider the honeycomb lattice resulting from the superposition of the two triangular lattices I and II as shown in figure 22a. In order to assign integer coordinates to each lattice site, we give an equivalent arangement of sites on a square lattice as shown in figure 22b. From these figures it can be observed that:

(i) If $S^{I}=\{\underline{s}\}$ is the set of position vectors of all the sites of the lattice when referred to a site of type I as the origin, then the set $S^{II}=\{-\underline{s}\}$, where $\underline{s}\in S^{I}$ is the set of position vectors of all the sites of the lattice when referred to a site of type II as the origin.

(ii) The probability that any step of a walker on the lattice results in a vector displacement $\underline{s}$ depends on whether the walker is occupying a site of type I or a site of type II.

Let $p^{I}(\underline{s})$ and $p^{II}(\underline{s})$ represent, respectively, the step probability functions when the walker is on a site of type I and when the walker is on a site of type II. $p^{I}(\underline{s})=p^{II}(-\underline{s})$ and, in particular, if the walker is only allowed to step to nearest sites with an equal probability to step to any of the three sites

$$p^{I}(\underline{s})=\begin{cases}\frac{1}{3} & \text{if } \underline{s}=(1,0),(-1,1),(0,-1)\\ 0 & \text{otherwise}\end{cases} \qquad (2.3.15)$$

$$p^{II}(\underline{\xi}') = \begin{cases} \frac{1}{3} & \text{if } \underline{\xi}' = (-1,0),(1,-1),(0,1) \\ 0 & \text{otherwise} \end{cases} \quad . \qquad (2.3.16)$$

We restrict ourselves now to walks starting from the origin only, which is chosen as a site of type I. If $P_n(\underline{\xi})$ is the probability that the walker is at site $\underline{\xi}$ after the n-th step, then the $\{P_n(\underline{\xi})\}$ satisfy the recursion formulae

$$P_{n+1}(\underline{\xi}) = \sum_{\underline{t}} p^{II}(\underline{\xi}-\underline{t}) P_n(\underline{t}) \qquad (2.3.17)$$

If $\underline{\xi}$ is a site of type I, and

$$P_{n+1}(\underline{\xi}) = \sum_{\underline{t}} p^{I}(\underline{\xi}-\underline{t}) P_n(\underline{t}) \qquad (2.3.18)$$

If $\underline{\xi}$ is a site of type II. Furthermore, by introducing the Fourier expansions

$$\lambda(\underline{\theta}) = \sum_{\underline{\xi}} p^{I}(\underline{\xi}) e^{i\underline{\xi}\cdot\underline{\theta}} = \frac{1}{3}\left(e^{i\theta_1} + e^{-i\theta_2} + e^{-i(\theta_1-\theta_2)}\right), \qquad (2.3.19)$$

$$\bar{\lambda}(\underline{\theta}) = \sum_{\underline{\xi}'} p^{II}(\underline{\xi}') e^{i\underline{\xi}'\cdot\underline{\theta}} = \frac{1}{3}\left(e^{-i\theta_1} + e^{i\theta_2} + e^{i(\theta_1-\theta_2)}\right) \qquad (2.3.20)$$

and

$$V_n(\underline{\theta}) = \sum_{\underline{\xi}} P_n(\underline{\xi}) e^{i\underline{\xi}\cdot\underline{\theta}} \qquad (2.3.21)$$

we observe that

$$V_n(\underline{\theta}) = \left[\bar{\lambda}(\underline{\theta})\lambda(\underline{\theta})\right]^{\frac{n}{2}} \quad \text{for even } n \qquad (2.3.22)$$

and

$$V_n(\underline{\theta}) = \lambda(\underline{\theta})\left[\bar{\lambda}(\underline{\theta})\lambda(\underline{\theta})\right]^{\frac{n-1}{2}} \quad \text{for odd } n \, . \qquad (2.3.23)$$

The Fourier expansion $U(\underline{\theta}; z_1)$ of the lattice Green's function $P(\underline{\xi}; z_1) = \sum_n P_n(\underline{\xi}) z_1^n$ becomes

$$U(\underline{\theta}; z_1) = (1+\lambda z_1)\sum_{n=0} (\lambda\bar{\lambda} z_1^2)^n$$

$$= \frac{1+\lambda z_1}{1-z_1^2\lambda\bar{\lambda}} \, , \quad |z_1^2\lambda\bar{\lambda}| < 1 \, . \qquad (2.3.24)$$

For the particular walk we are considering, $P(\underline{\xi}; z_1)$ is a

series in even powers of z_1 when $\underline{s}$ is a site of type I, since all $P_{2n+1}(\underline{s})$ vanish (it is not possible to connect two sites of the same type by a walk with an odd number of steps). We have

$$P(\underline{s};z_1) = \sum_{n=0} P_{2n}(\underline{s})\, z_1^{2n} \tag{2.3.25}$$

If $\underline{s}$ is of type I. Similarly

$$P(\underline{s};z_1) = \sum_{n=0} P_{2n+1}(\underline{s})\, z_1^{2n+1} \tag{2.3.26}$$

if $\underline{s}$ is of type II. Or alternatively

$$P(\underline{s};z_1) = \begin{cases} \dfrac{1}{4\pi^2}\displaystyle\iint_{-\pi}^{\pi} \dfrac{e^{-i\underline{s}\cdot\underline{\theta}}}{1-z_1^2\lambda\bar{\lambda}}\, d\underline{\theta}\,, & \underline{s} \text{ of type I} \\ \dfrac{1}{4\pi^2}\displaystyle\iint_{-\pi}^{\pi} \dfrac{\lambda z_1 e^{-i\underline{s}\cdot\underline{\theta}}}{1-z_1^2\lambda\bar{\lambda}}\, d\underline{\theta}\,, & \underline{s} \text{ of type II.} \end{cases} \tag{2.3.27}$$

With regard to the inhomogeneous lattice gas (first neighbour interactions only) we obtain the familiar expressions

$$c_0^{(1)} = \frac{1}{\rho_1}\left\{1 - \frac{P(\underline{0};z_1)}{1-\rho_1}\right\} \tag{2.3.28}$$

$$c_0^{(2)} = \frac{1}{\rho_2}\left\{1 - \frac{P(\underline{0};z_1)}{1-\rho_2}\right\} \tag{2.3.29}$$

$$c_1^{(3)} = \frac{z_1}{3[\rho_1\rho_2(1-\rho_1)(1-\rho_2)]^{\frac{1}{2}}}\, P(\underline{0};z_1) \tag{2.3.30}$$

$$h^{(ij)}(\underline{s}) = \left[\frac{(1-\rho_i)(1-\rho_j)}{\rho_i\rho_j}\right]^{\frac{1}{2}} F(\underline{s};z_1) \tag{2.3.31}$$

where

$$c_0^{(1)} = c^{(11)}(0,0)$$
$$c_0^{(2)} = c^{(22)}(0,0)$$
$$c_1^{(3)} = c^{(12)}(1,0) = c^{(12)}(-1,1) = c^{(12)}(0,-1)$$
$$= c^{(21)}(-1,0) = c^{(21)}(1,-1) = c^{(21)}(0,1)$$

and $$F(\underline{\sigma};z_1) = \frac{P(\underline{\sigma};z_1) - \delta_{\underline{\sigma},\underline{\varrho}}}{P(\underline{\varrho};z_1)} \quad .$$

The solutions for the sublattice densities and the behaviour of the weight factor and the correlation functions are similar to those found for the SQ1 model. The transition density for the hard-core model has the value $\rho = 0.33$, slightly higher than the value found for the PY SQ1 analogue, but substantially lower than the value obtained from the transfer matrix method results for this model[40].

2.4 SUMMARY

We have selected a few lattice gas models to illustrate how different aspects of the behaviour of the lattice gas can be discussed in terms of the general formalism developed in the previous chapter.

The L1 model is a particularly transparent example to look at the basic properties of the weight function and the correlation functions of the fluid phase of a lattice gas. Rigorous closed-form expressions are derived for the hard-core L1 model.

To study the effect of extending the range of the potential function we chose the L12 model. The extension to second-nearest neighbours is clearly reflected in the oscillatory character of the total correlation function of the hard-core L12 model. However the range of the interaction is not long enough to produce monotonic decay in $h(s)$ for the L12 model with attraction.

The most interesting feature of the hard-core SQ1 model is its order-disorder transition. When treated under the PY approximation it appears in the form of a second-order Enrenfest phase transition, in contrast with the continuous transition that more exact methods predict for this model. We evaluate and compare the weight functions behind each type of transition.

The duplication of phase transitions due to softness of the hard core is studied in the SQ1 model with finite interactions. This property, first explained in terms of the particle-hole symmetry of the lattice gas, is not suppressed by the employment of the PY approximation. It does, however, appear somewhat distorted and both transitions are of the second-order-Ehrenfest type.

Finally, we consider the honeycomb lattice gas to illustrate how the method can be extended to include lattices with different geometries.

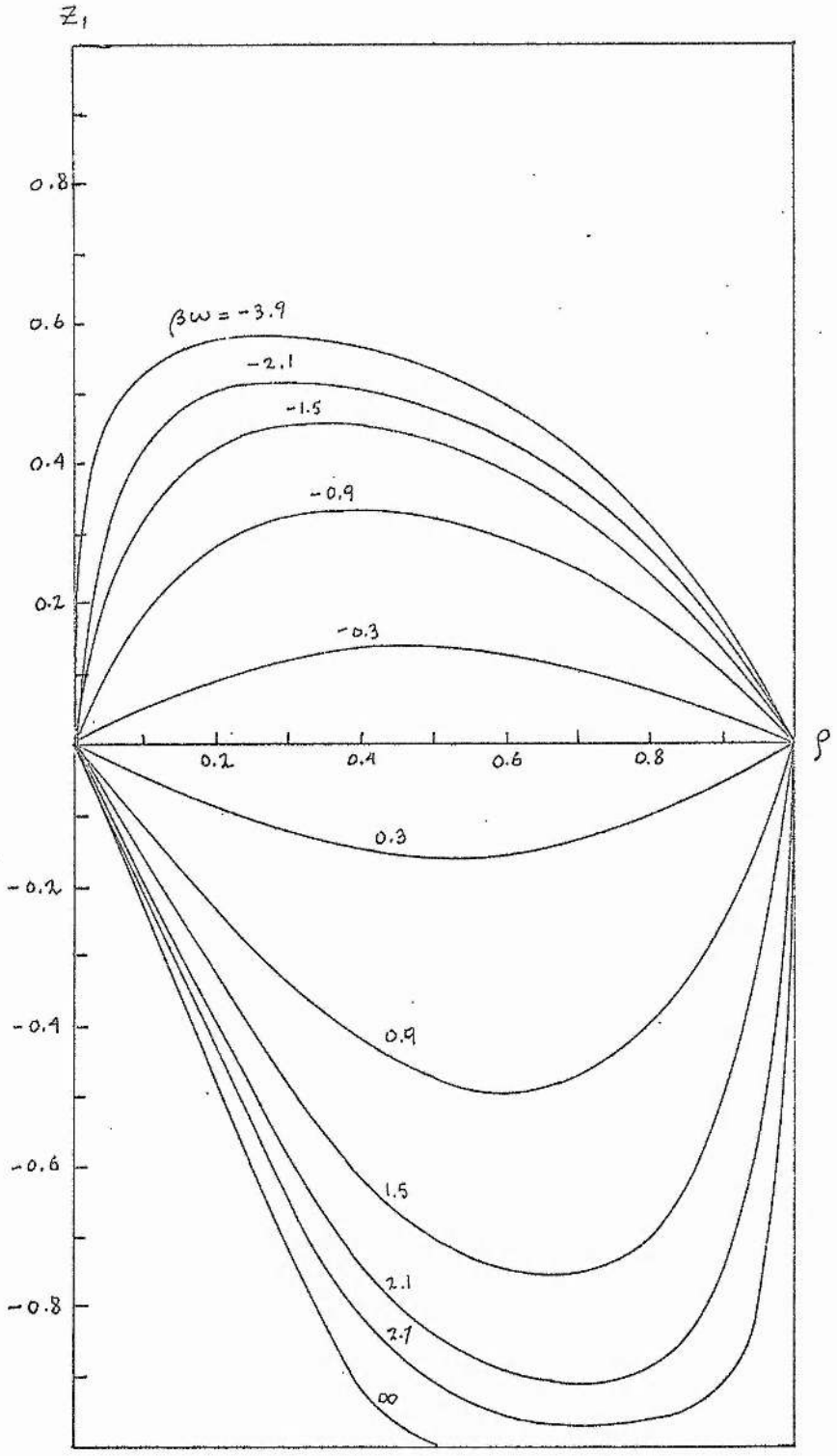

Figure 1. L1 model.

The weight factor $\mathcal{Z}_1$ at different temperatures as function of density for both attractive and repulsive interactions. β is the inverse product of the Boltzmann constant and temperature, ω is the interaction.

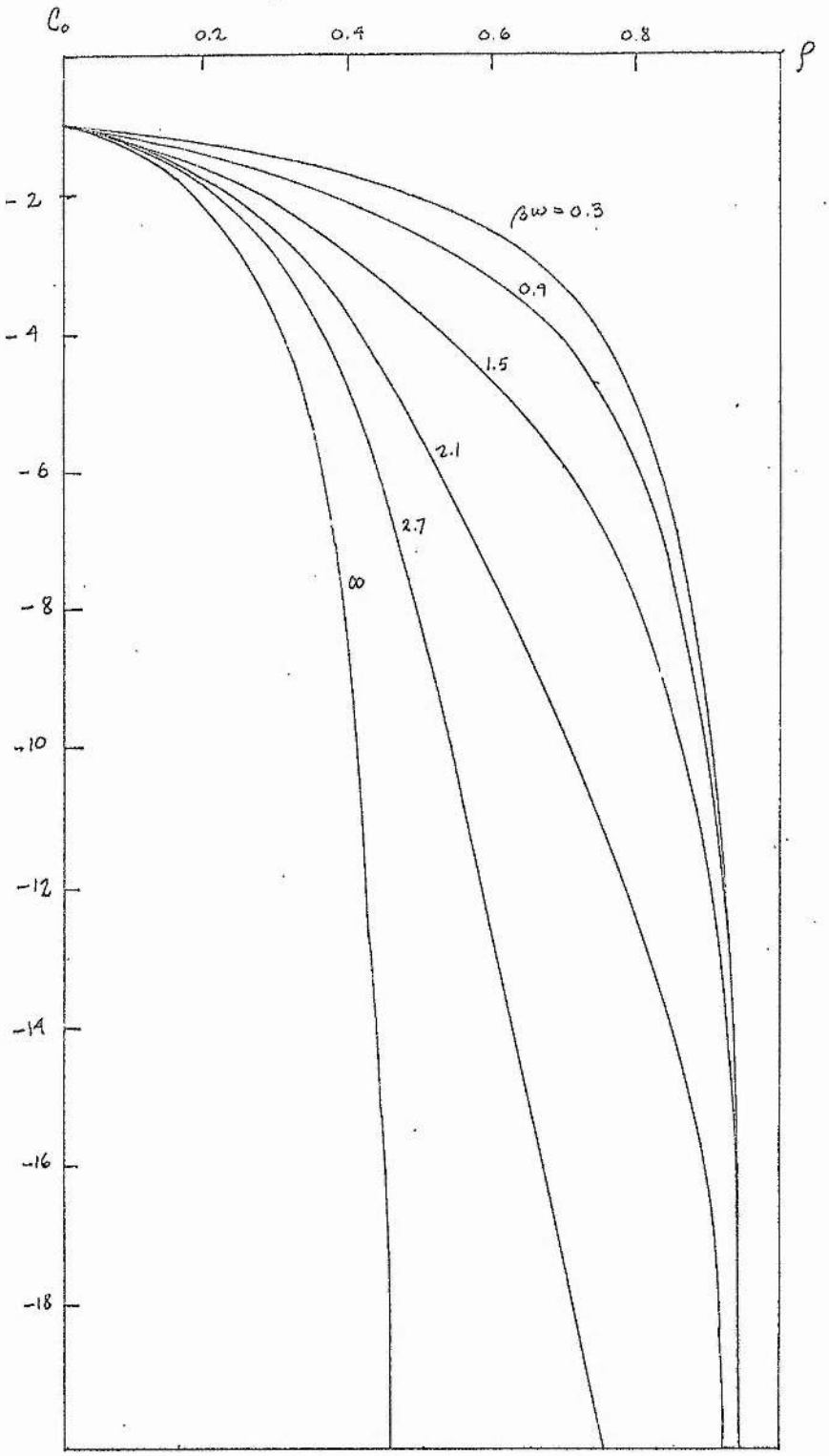

Figure 2. L1 model.

The direct correlation function at $s=0$ as a function of density for repulsive interactions.

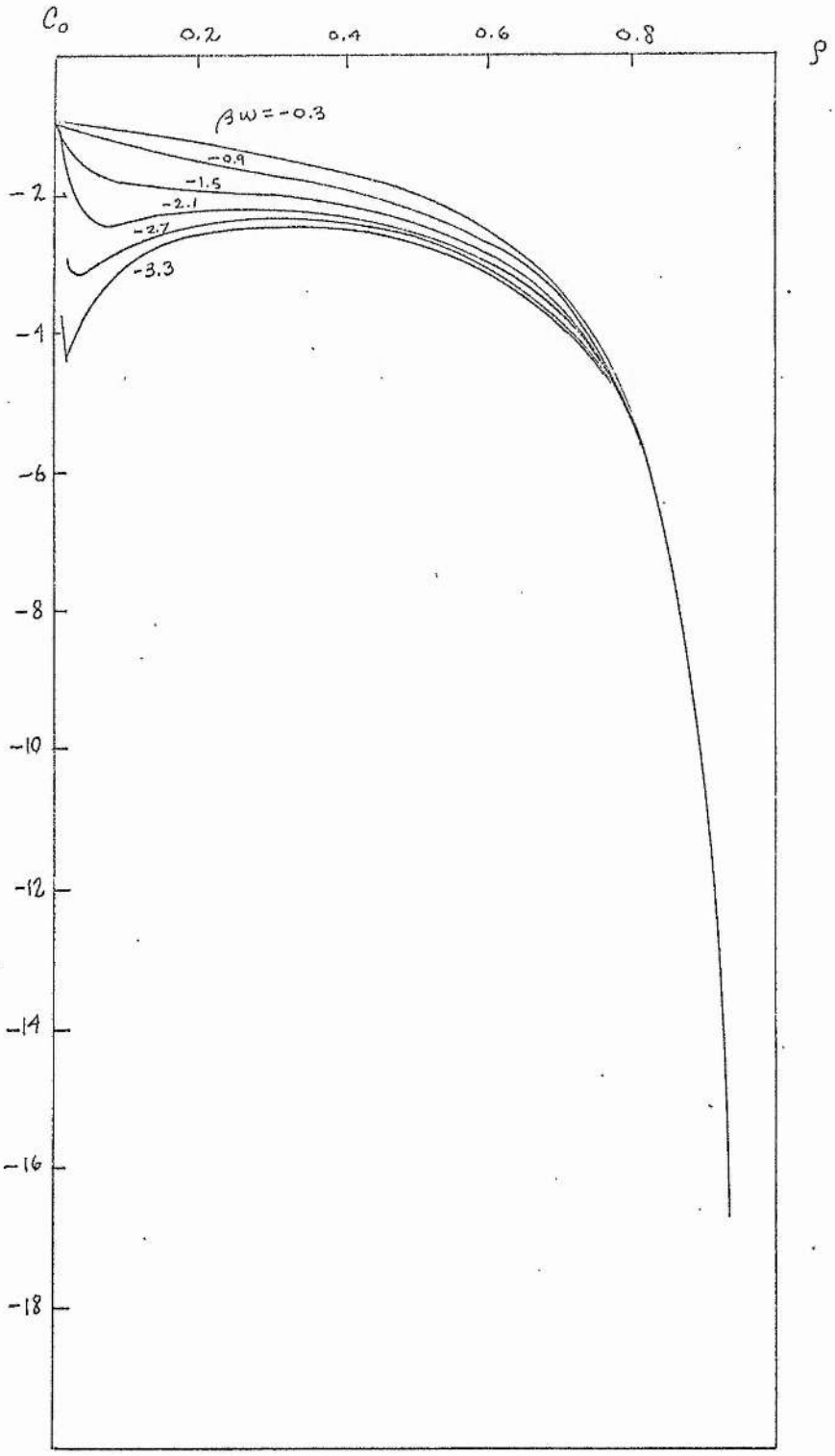

Figure 3. L1 model.

The direct correlation function at $s=0$ as a function of density for attractive interaction.

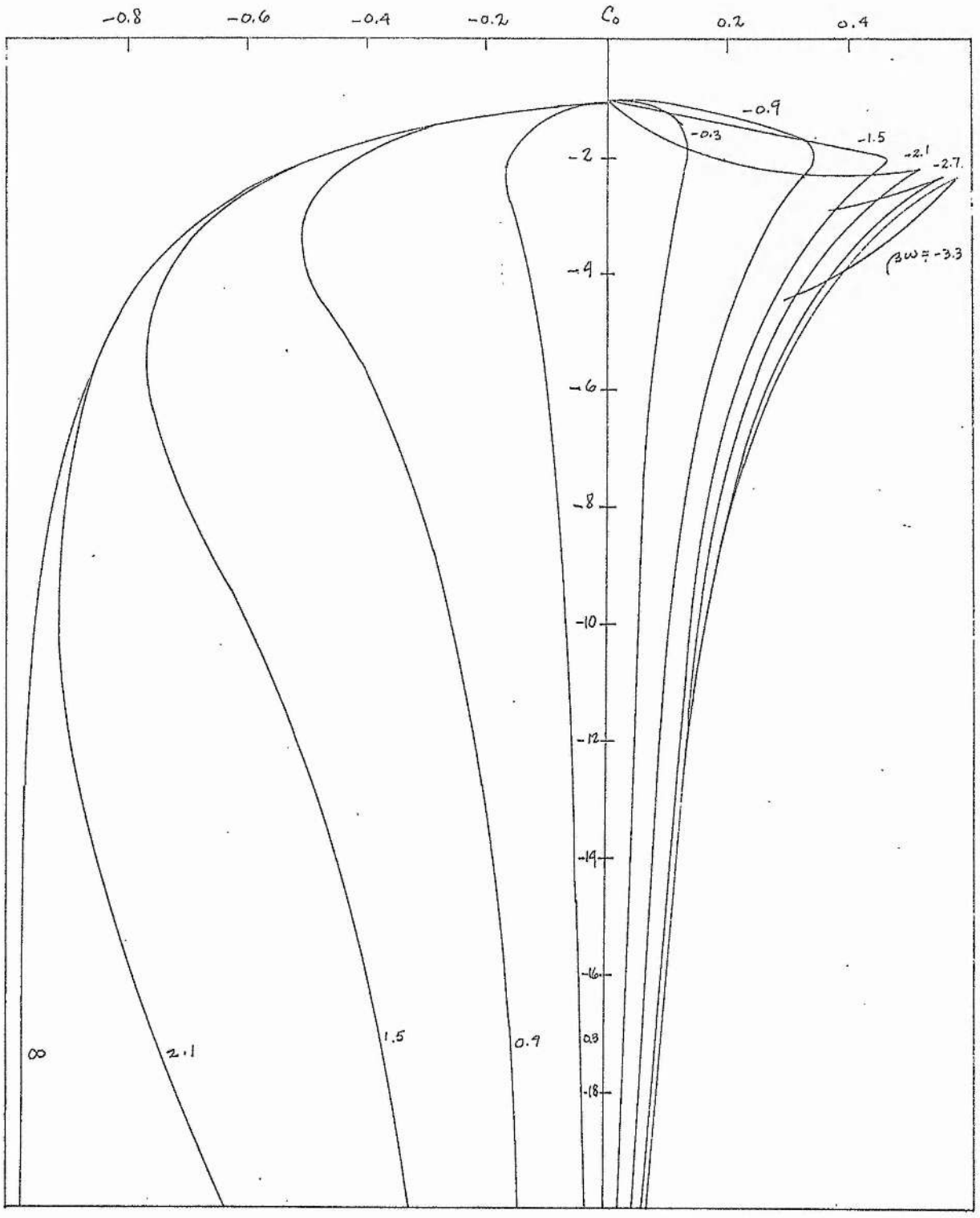

Figure 4. L1 model.

The dependence of the direct correlation function at $s=0$ on the weight factor Z_1 .

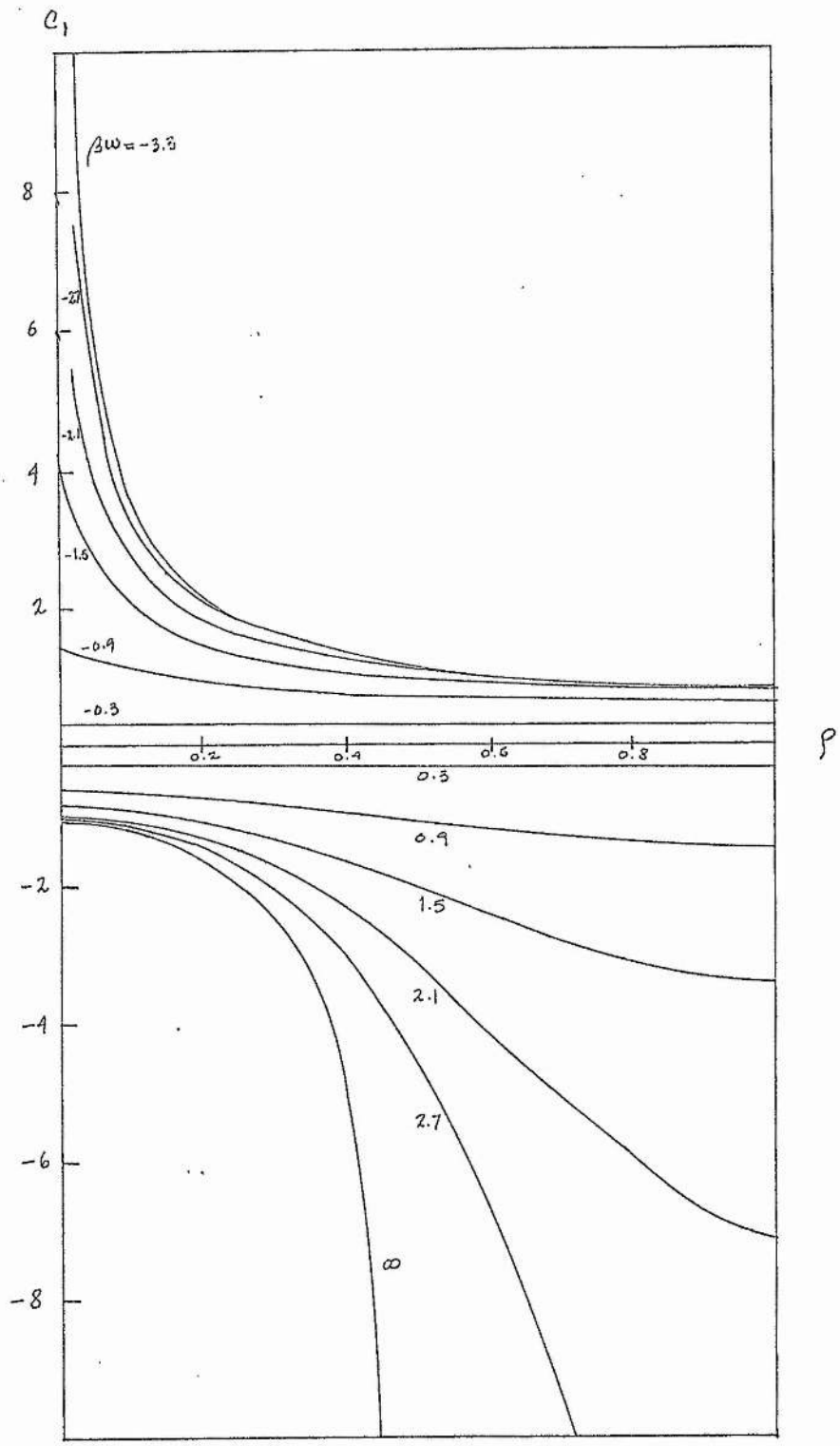

Figure 5. L1 model.

The direct correlation function for nearest-neighbours as a function of density.

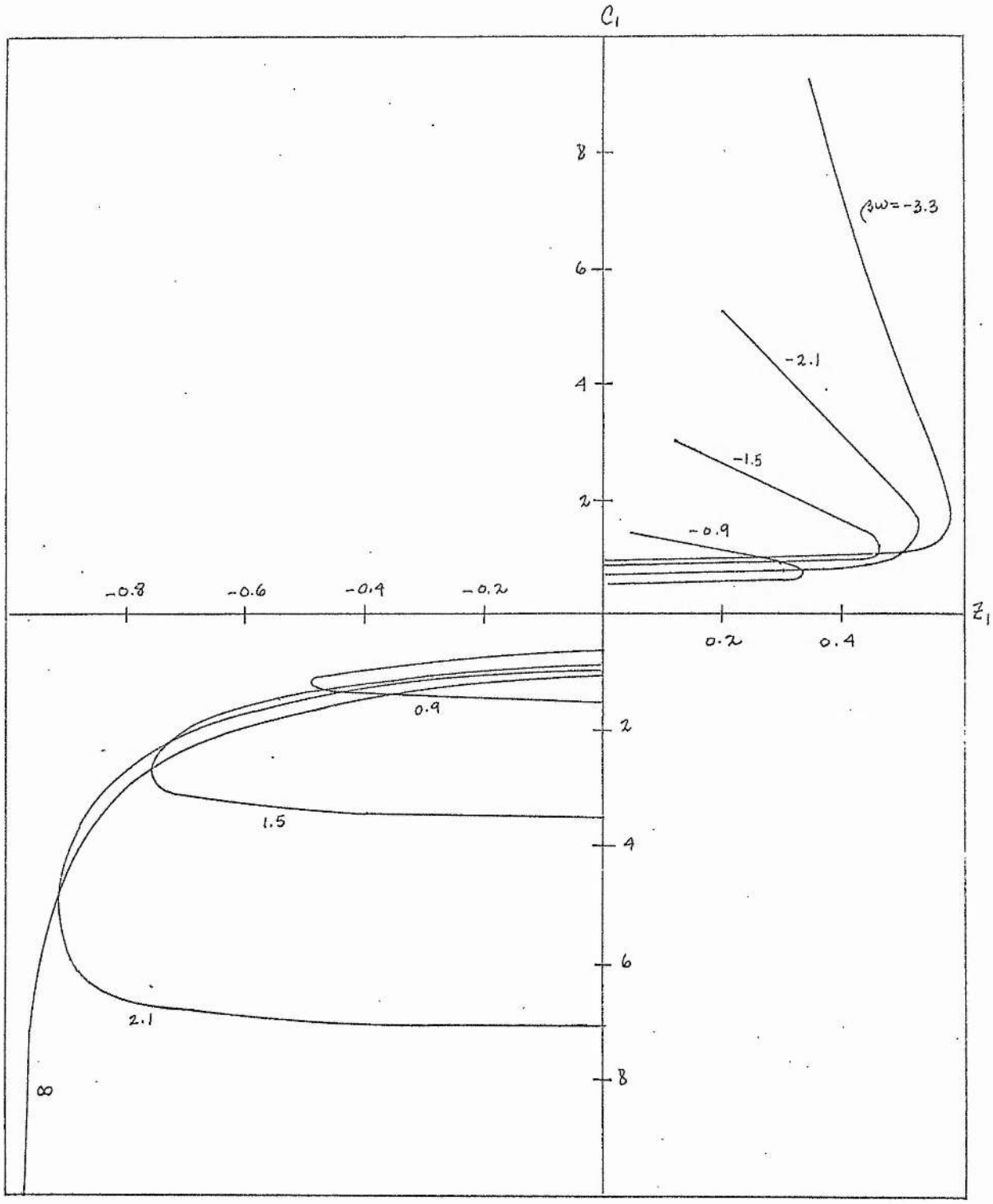

Figure 6. L1 model.

The dependence of the direct correlation function for nearest-neighbours on the weight factor z_1.

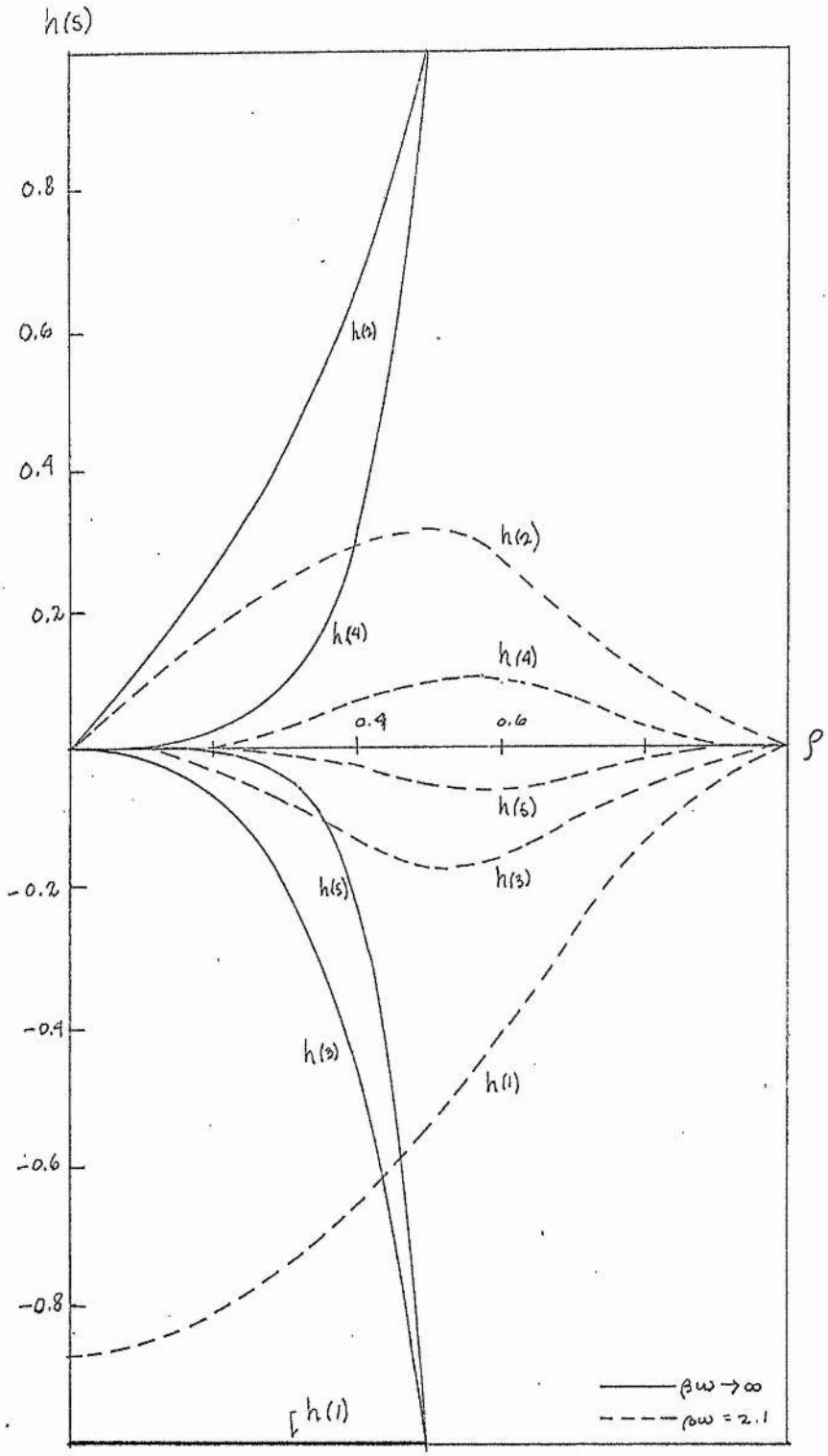

Figure 7. L1 model.

The total correlation function as a function of density for both infinite and soft repulsion.

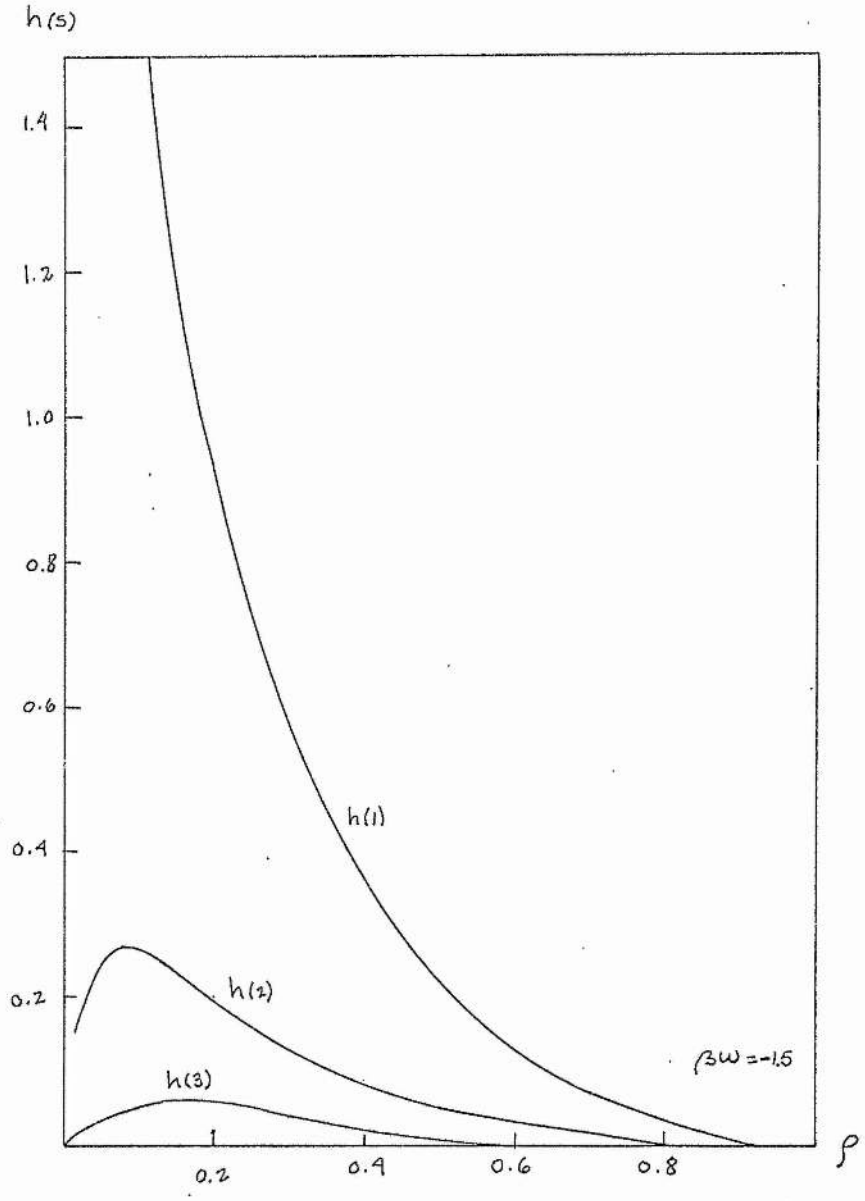

Figure 8. L1 model.

The total correlation function as a function of density for attractive interaction.

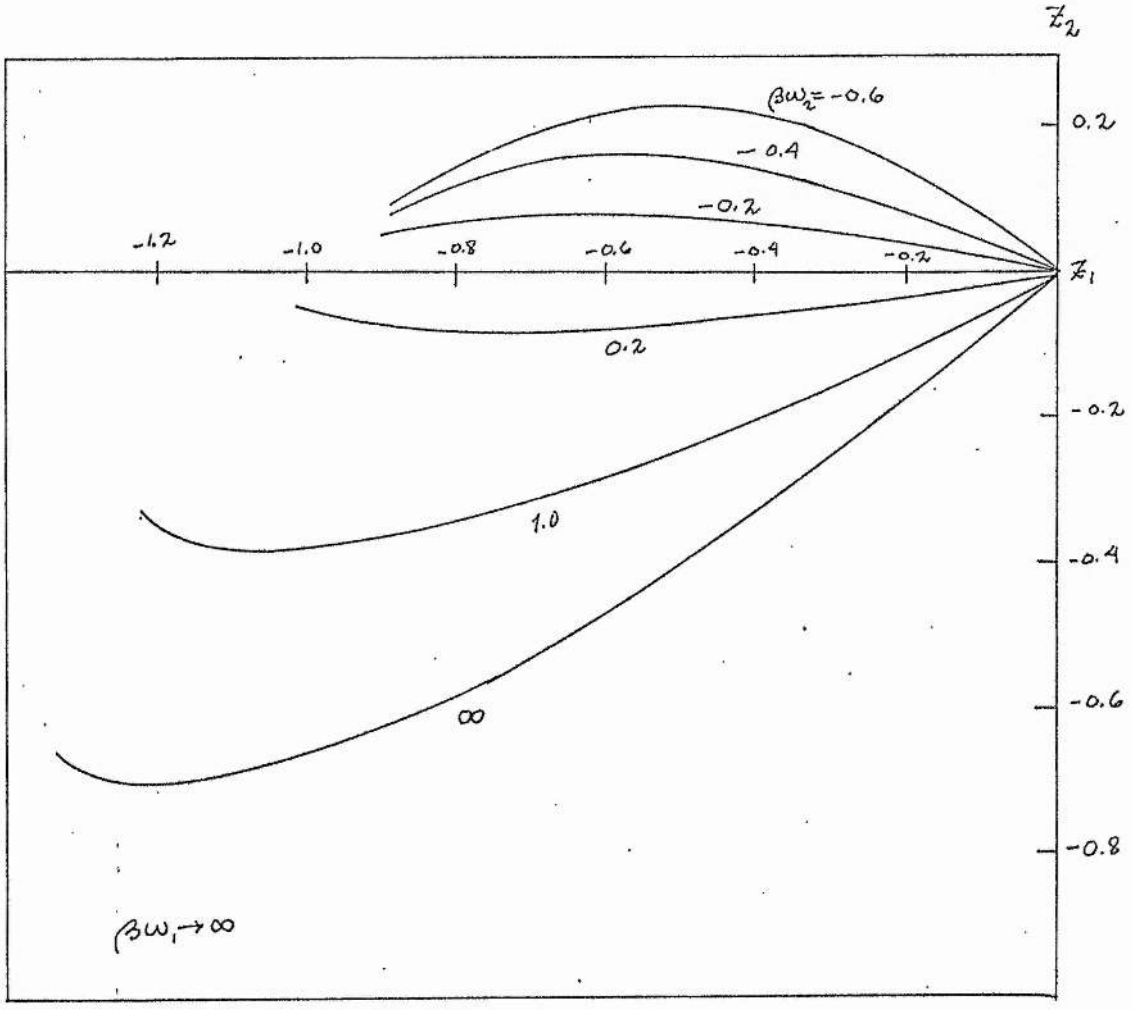

Figure 9. L12 model.

The weight factors for nearest-neighbour infinite repulsion and for both attractive and repulsive next-to-nearest neighbour interaction.

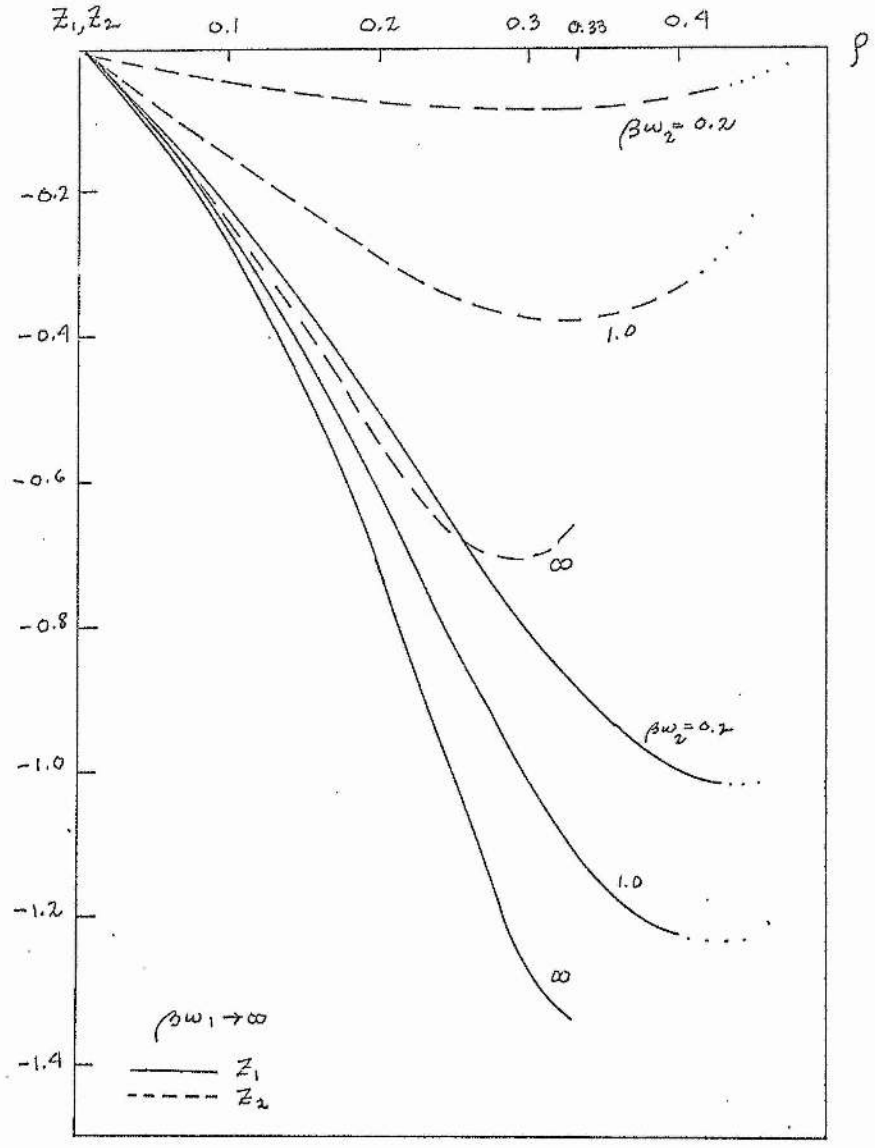

Figure 10. L12 model.

The weight factors as a function of density

for next-to-nearest-neighbour repulsive interaction.

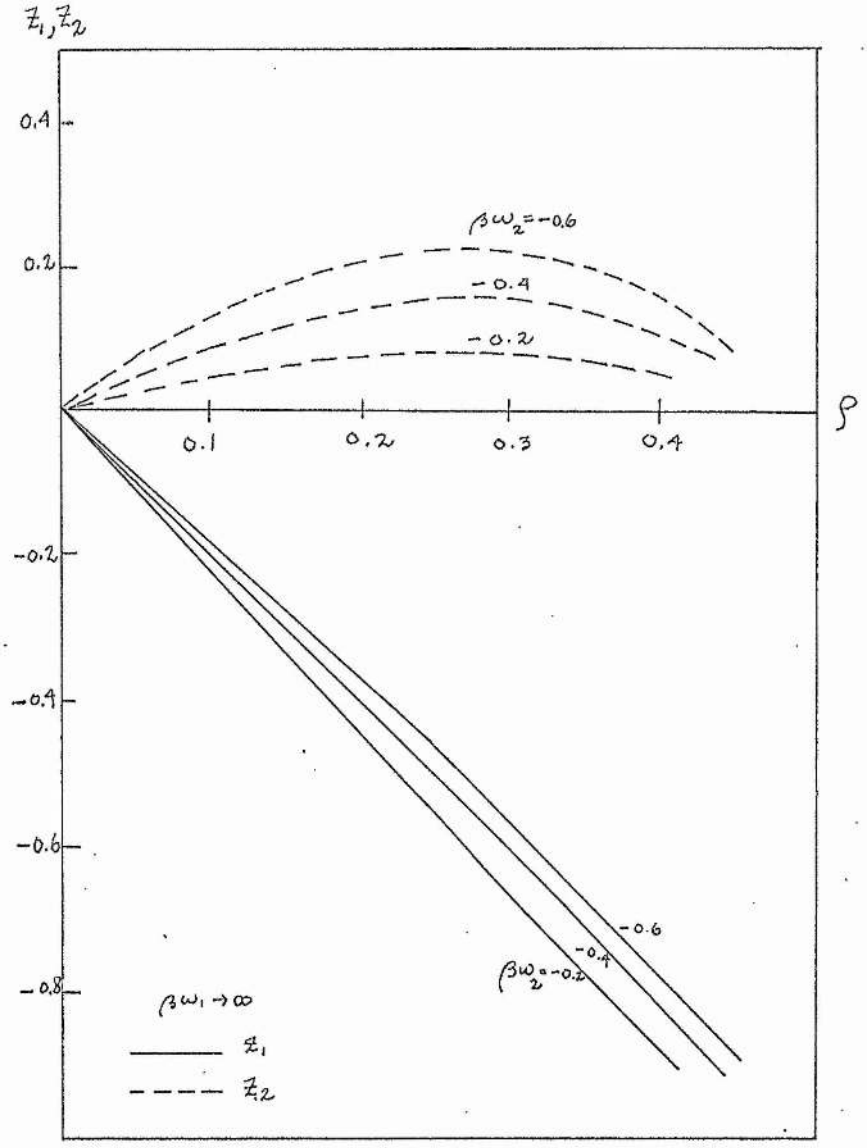

Figure 11. L12 model.

The weight factors as a function of density for next-to-nearest-neighbour attraction.

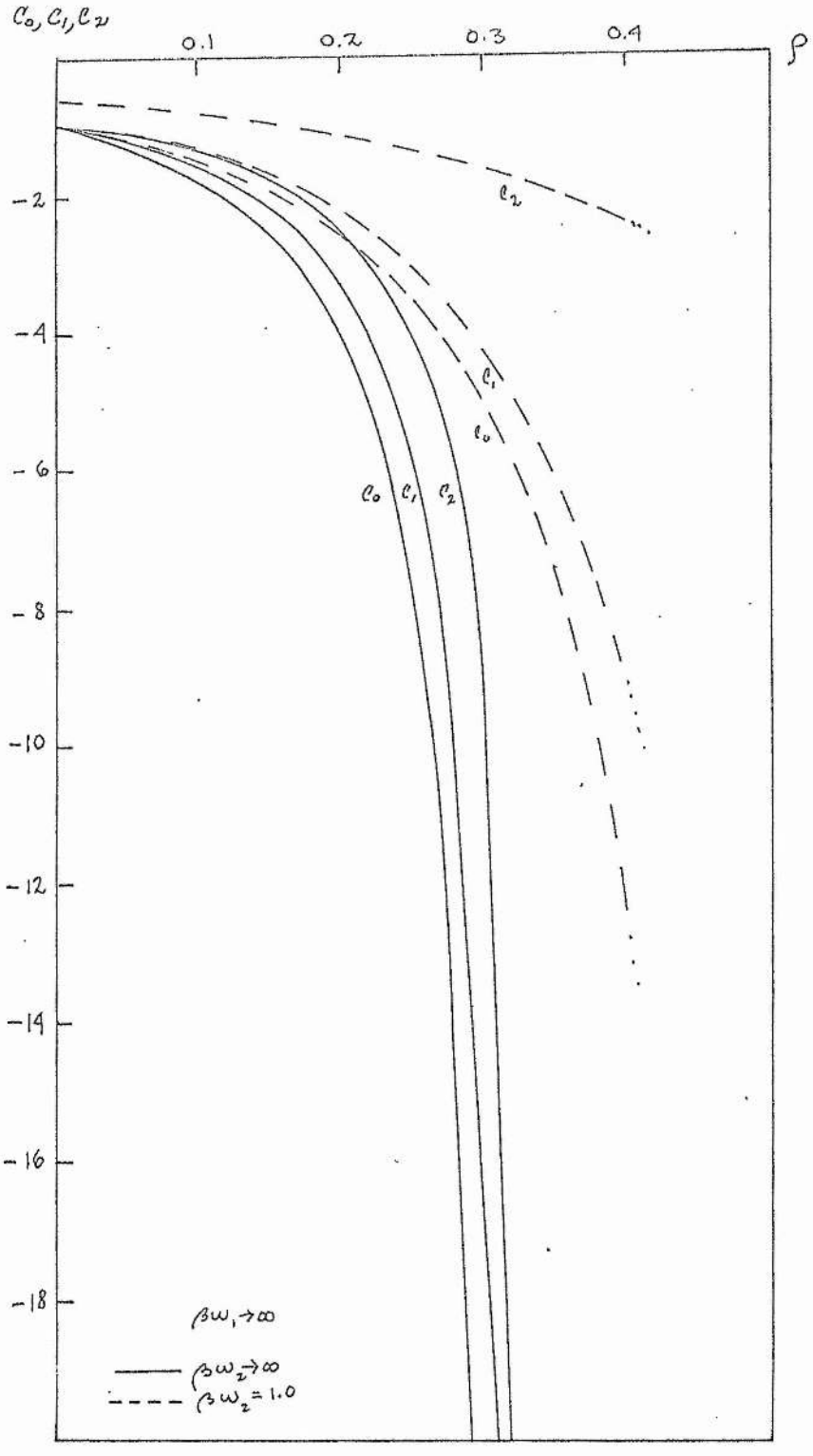

Figure 12. L12 model.

The direct correlation function against density for repulsive interactions.

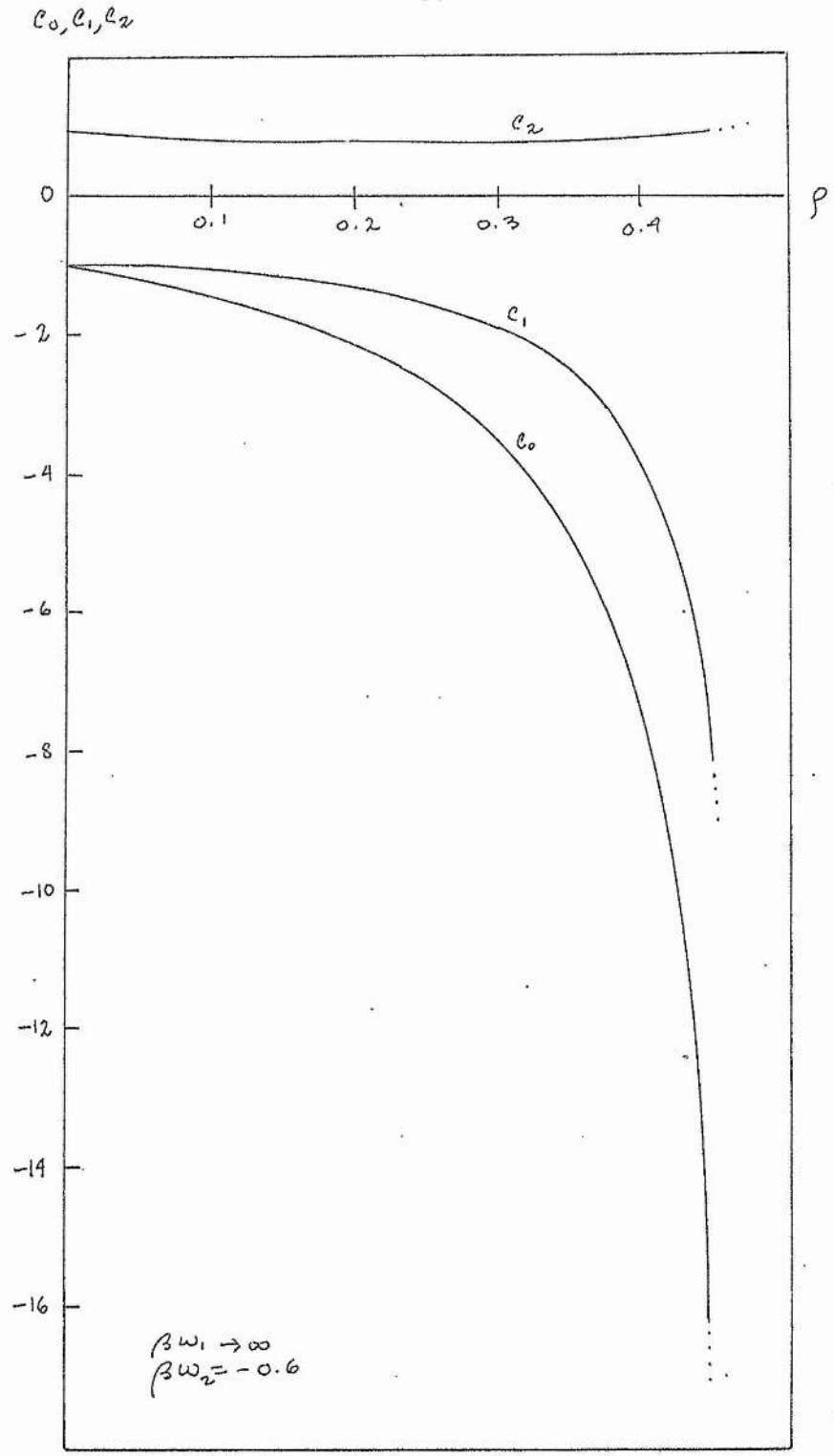

Figure 13. L12 model.

The direct correlation function for next-to-nearest-neighbour attraction.

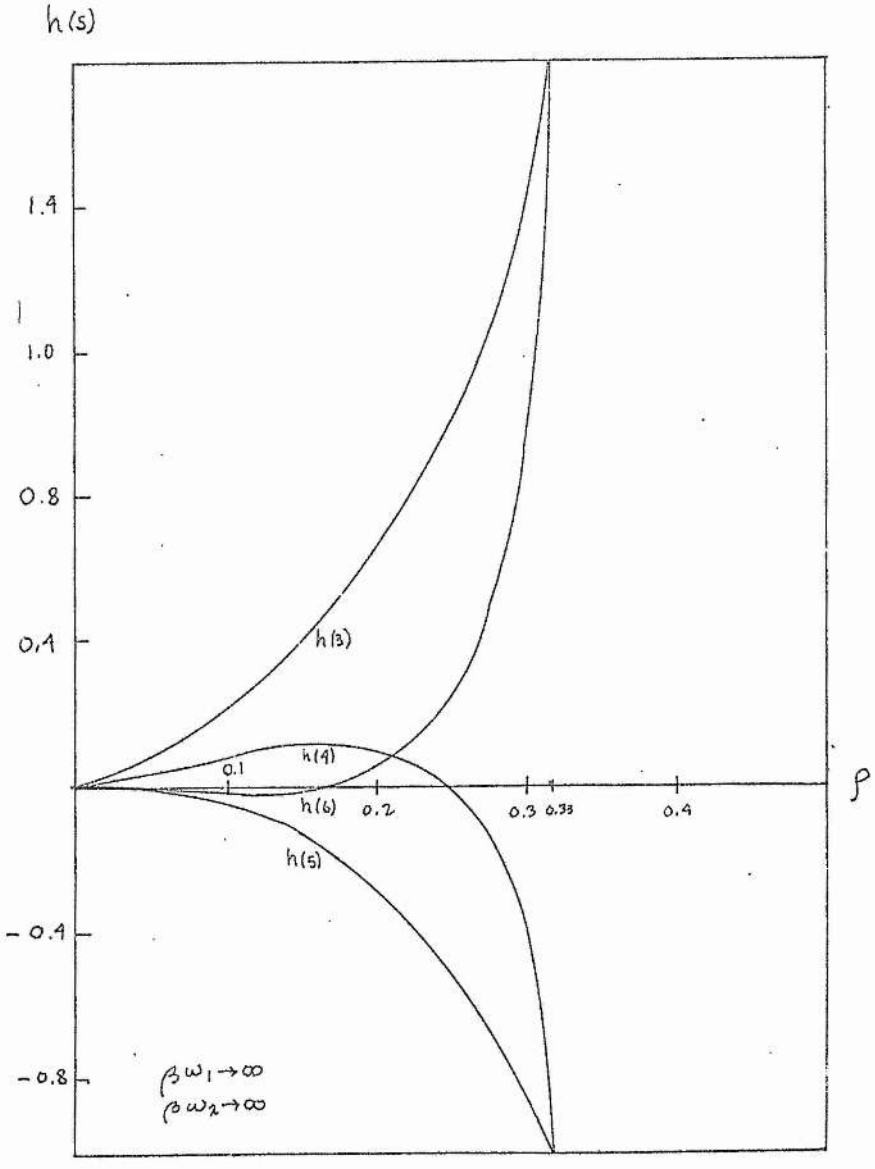

Figure 14. L12 model.

The total correlation function for nearest- and next-to-nearest-neighbour exclusion.

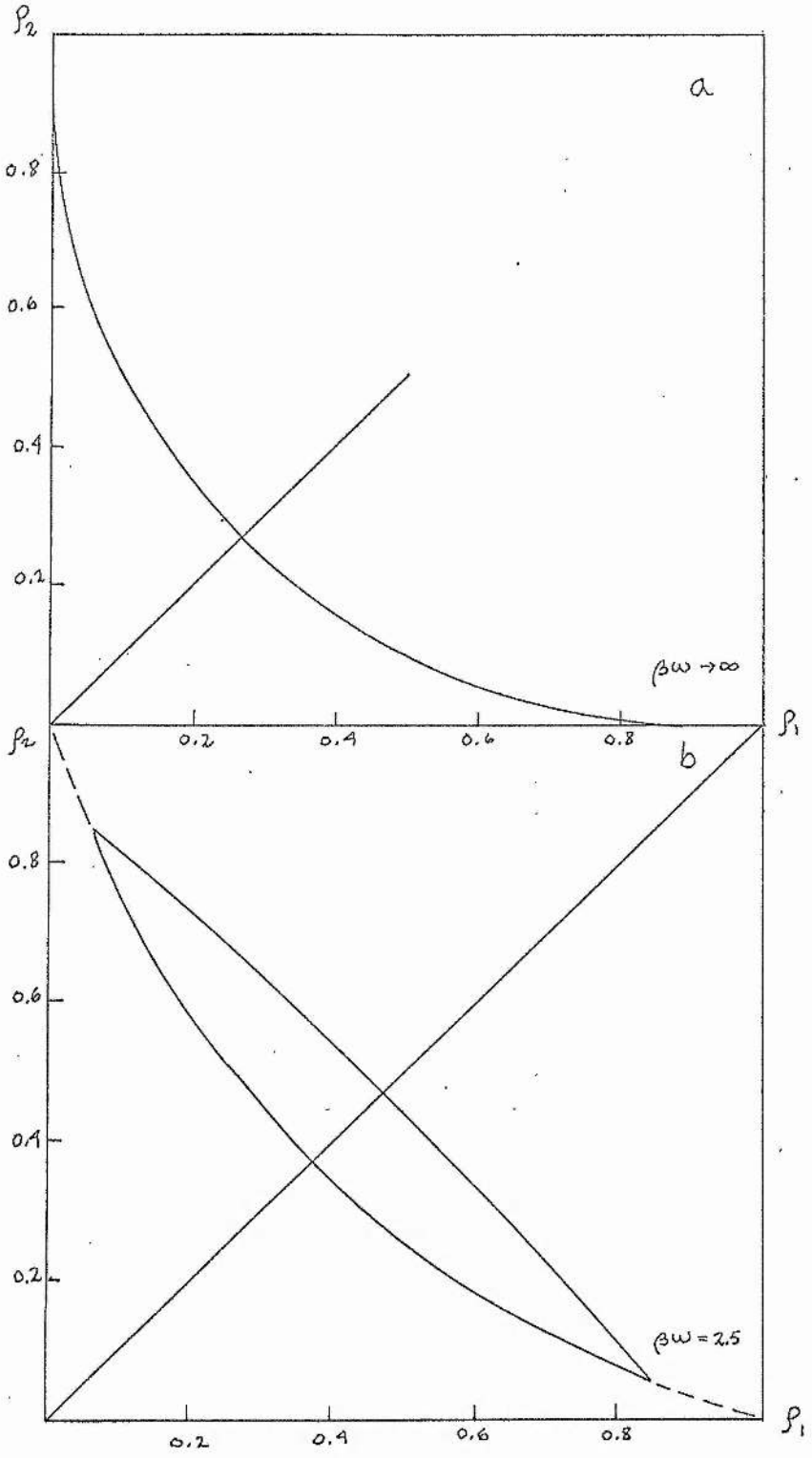

Figure 15. SQ1 model.

The sublattice densities solutions for a) infinite repulsion and b) soft repulsion ($\beta\omega = 2.5$).

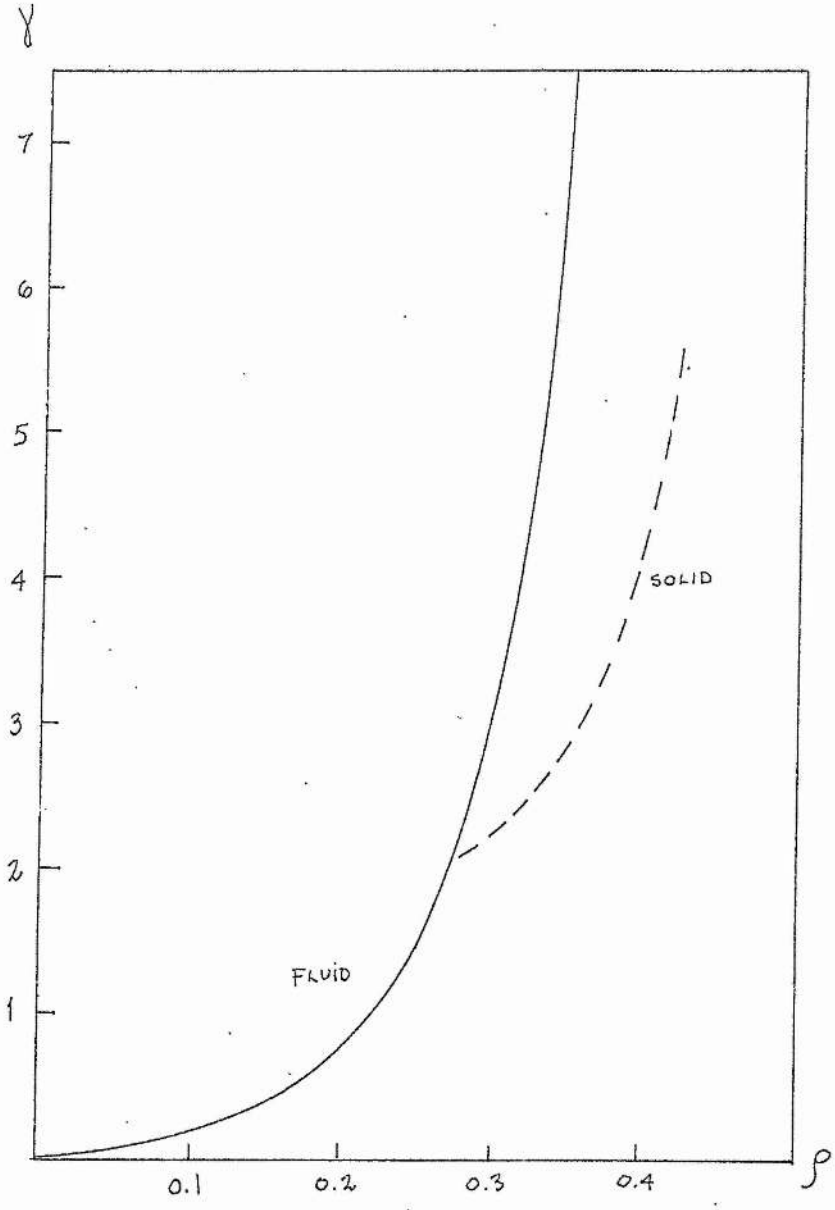

Figure 16. SQ1 model.

Infinite repulsion. Activity against density.

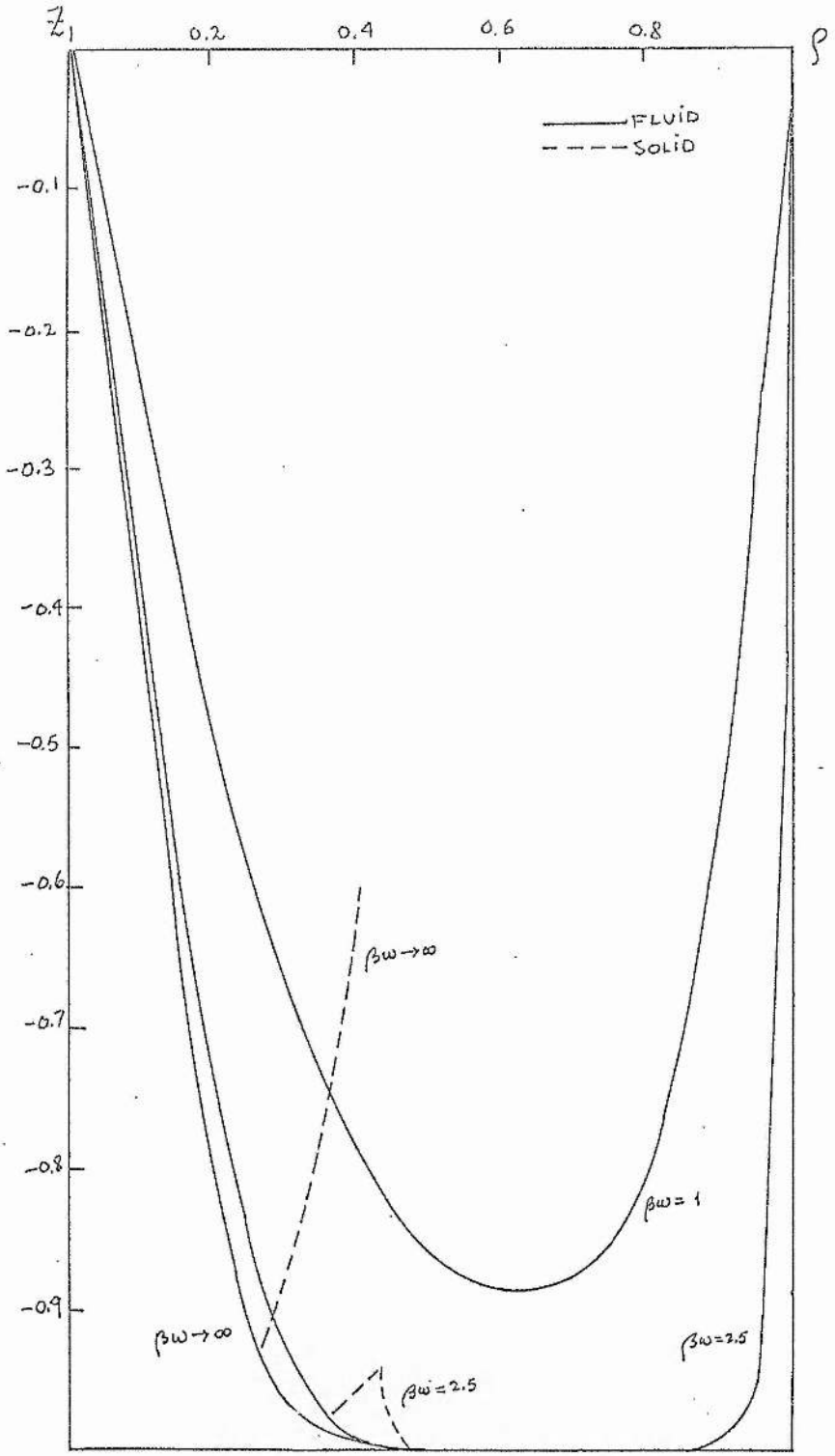

Figure 17. SQ1 model.

The weight factor as function of density for infinite repulsion (one solid phase), soft repulsion at low temperature (two solid phases) and soft repulsion at high temperature (no solid phase).

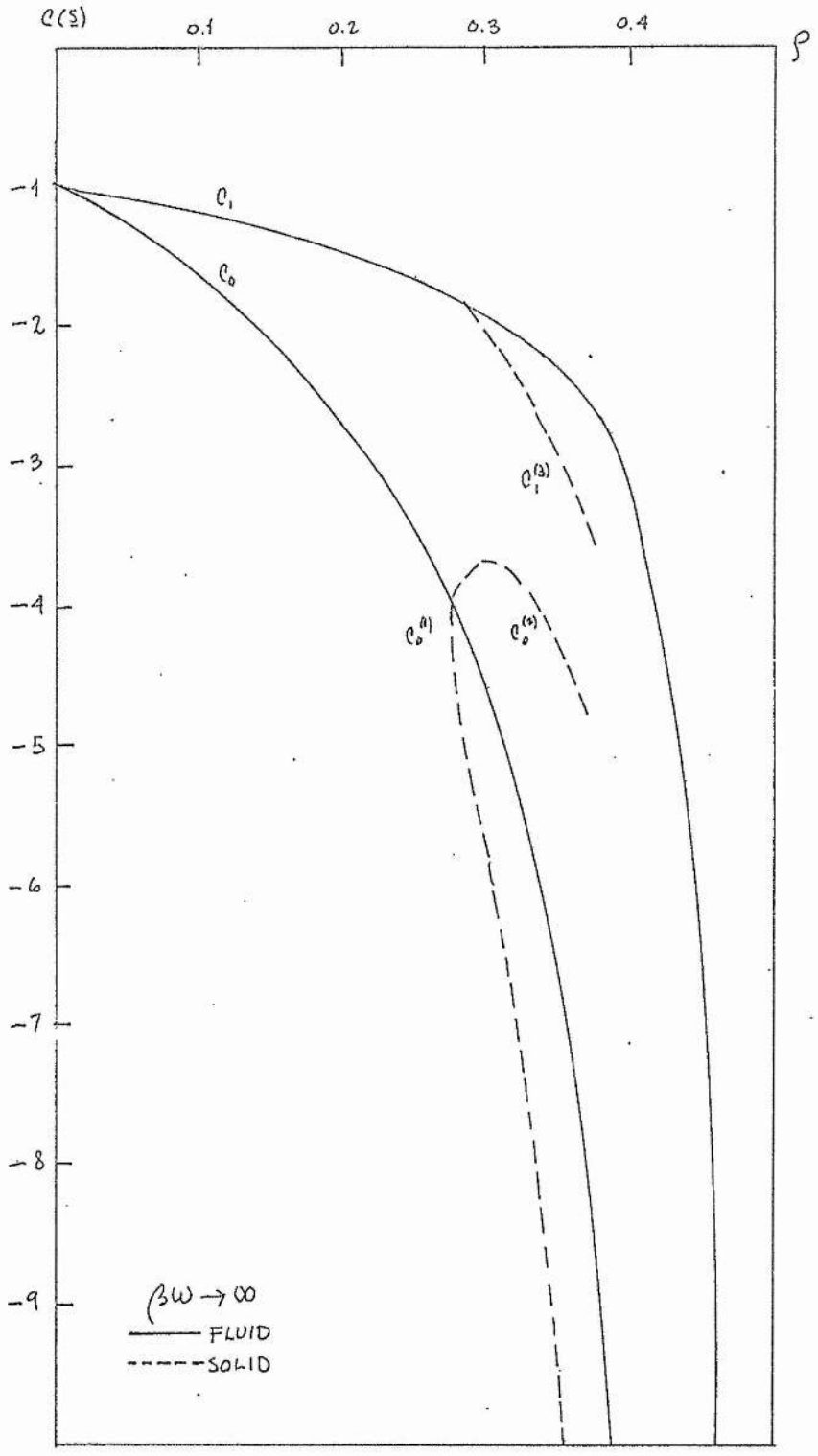

Figure 18. SQ1 model.

Infinite repulsion. The direct correlation function of both fluid and solid phases.

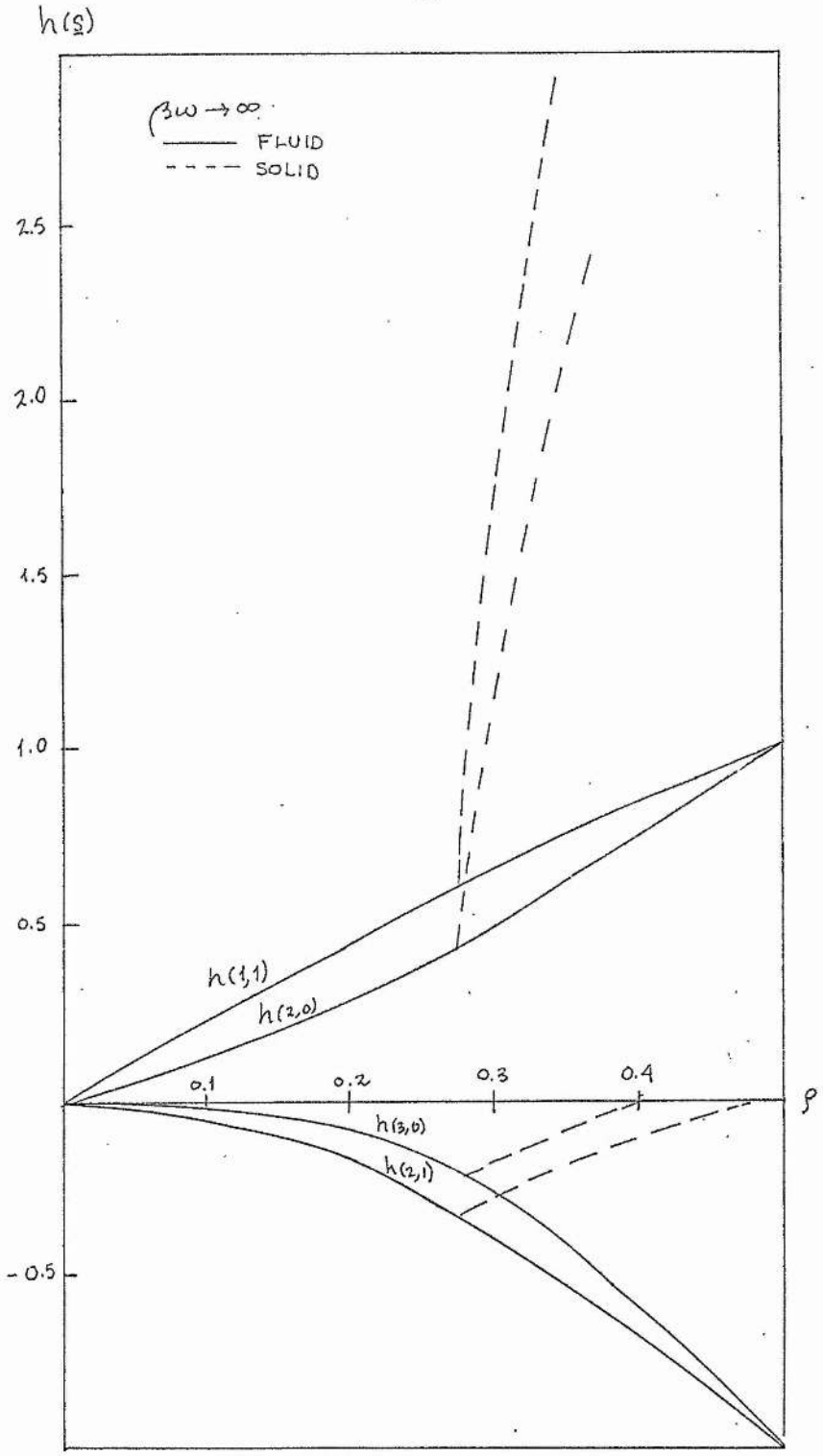

Figure 19. SQ1 model.

Infinite repulsion. The total correlation function for the fluid phase and for one solid branch.

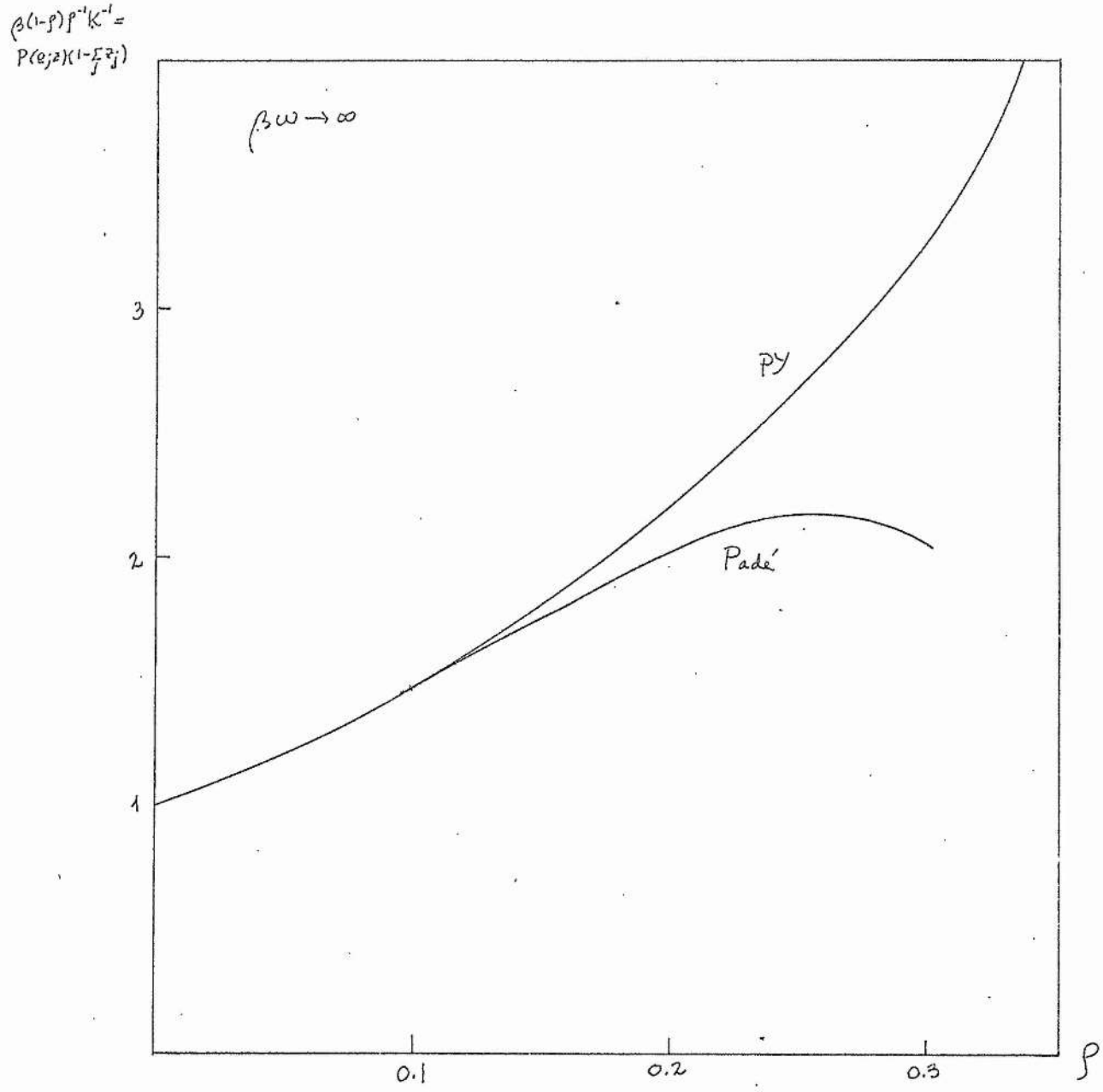

Figure 20. SQ1 model.

Infinite repulsion. The quantity $\beta(1-\rho)\rho^{-1}K^{-1}$ for the fluid phase as given by the PY approximation and from Padé approximant data[33]. K is the isothermal compressibility (see equation (1.3.21)).

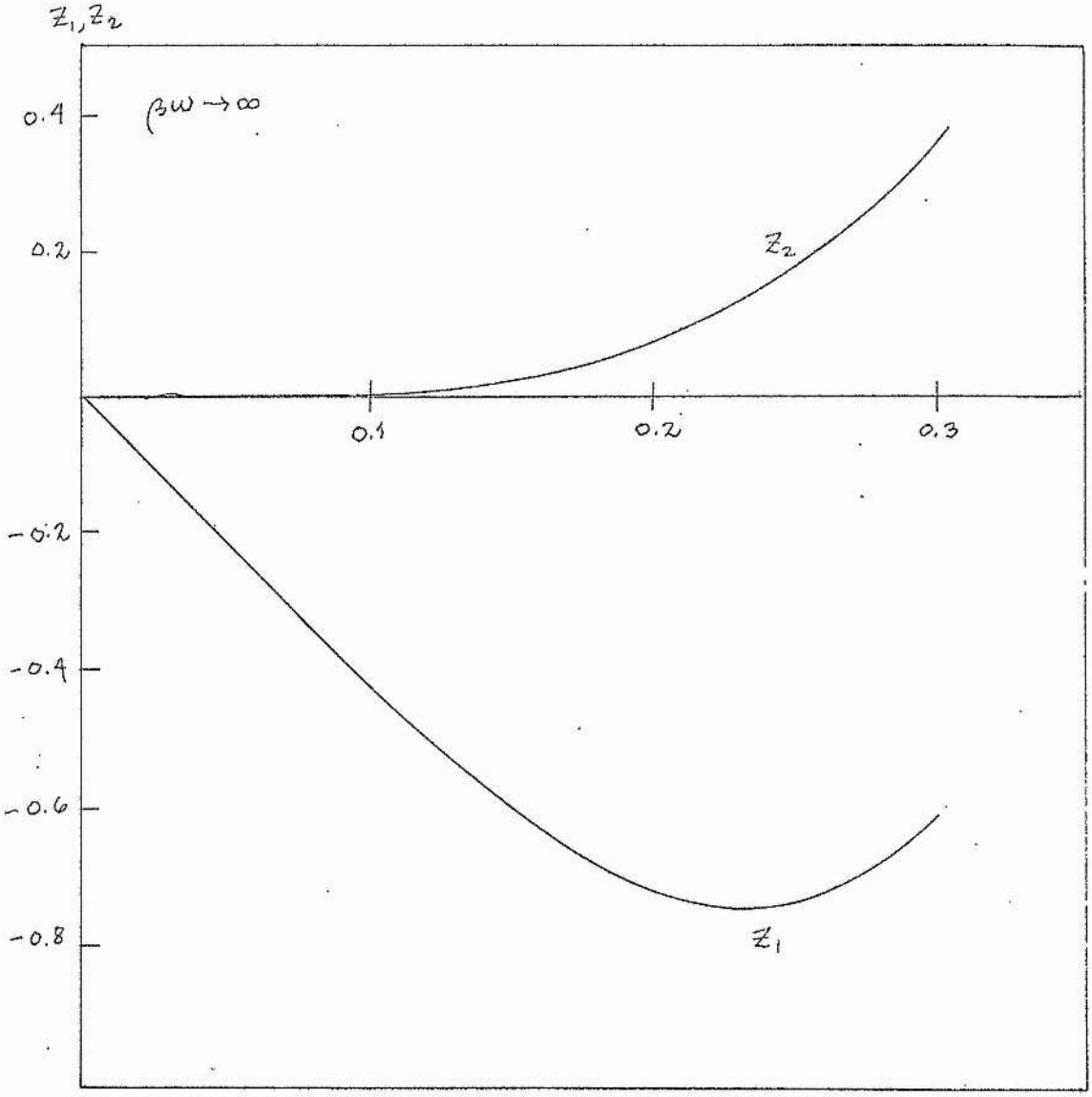

Figure 21. SQ1 model.

Infinite repulsion. The weight factors z_1 and z_2 that reproduce the Padé approximant data for the isothermal compressibility.

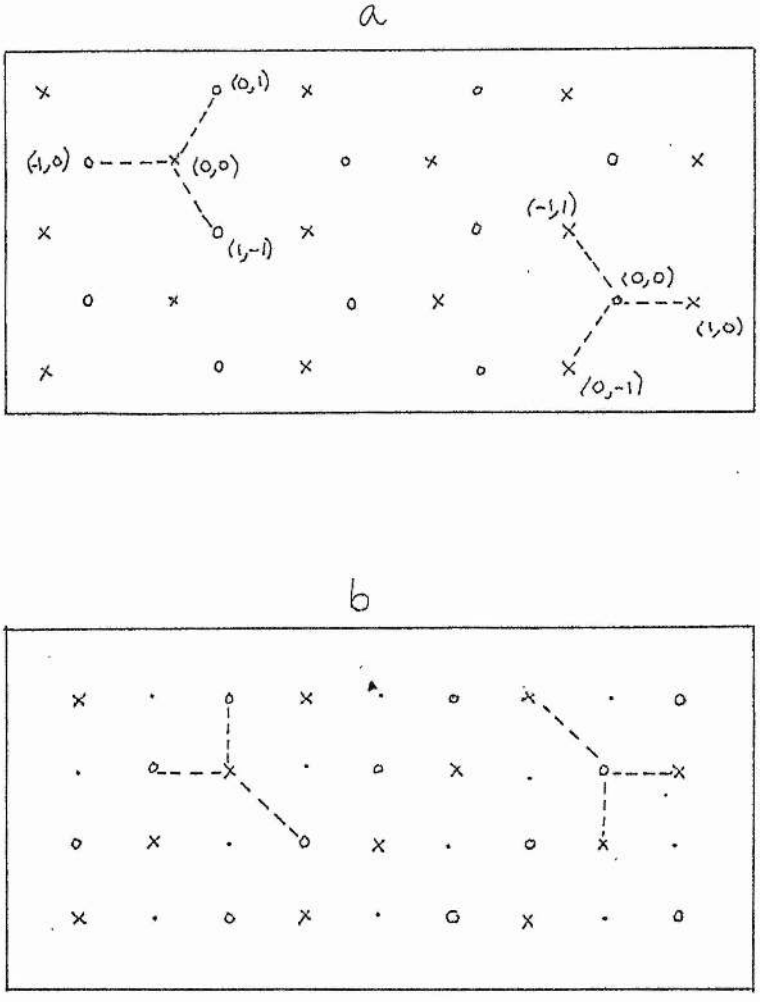

Figure 22.

a) Sublattice arrangement for the honeycomb lattice.

b) Equivalent site arrangement in the square lattice.

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